

**STABILITY ENHANCING FORMULATION COMPONENTS,  
COMPOSITIONS AND LAUNDRY METHODS EMPLOYING SAME**

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Related Applications

10 This application is a continuation under 35 USC §120 of PCT International Application  
Serial No. US00/23319 filed August 25, 2000, published in accordance with PCT article 21(2) in  
English, which claims priority to Provisional Application Serial Nos. 60/151,172 filed August 27,  
1999 and 60/151,216 filed August 27, 1999.

Field of the Invention

15 This present invention relates to compositions containing organic catalyst compounds,  
preferably branched organic catalysts, such as bleach boosting compounds, bleaching species,  
modified amines and modified amine oxides, sulfonimines, phosphonimines, N-acylimines and  
thiodiazole dioxides in combination with anionic surfactants, and laundry methods employing  
20 same that provide effective bleaching of fabrics and increased resistance to decomposition of the  
organic catalyst compounds. More particularly, this invention relates to compositions comprising  
quaternary imine bleach boosting compounds, quaternary oxaziridinium bleaching species, and/or  
modified amines modified amine oxide compounds, sulfonimines, phosphonimines, N-acylimines  
and/or thiodiazole dioxides and anionic surfactants, and laundry methods employing same.

Background of the Invention

25 Oxygen bleaching agents have become increasingly popular in recent years in household  
and personal care products to facilitate stain and soil removal. Bleaches are particularly desirable  
for their stain-removing, dingy fabric cleanup, whitening and sanitization properties. Oxygen  
bleaching agents have found particular acceptance in laundry products such as detergents, in  
30 automatic dishwashing products and in hard surface cleansers. Oxygen bleaching agents,  
however, are somewhat limited in their effectiveness. Some frequently encountered disadvantages  
include their lack of fabric color safety and their tendency to be extremely temperature rate  
dependent. Thus, the colder the solution in which they are employed, the less effective the  
bleaching action. Temperatures in excess of 60 °C are typically required for effectiveness of an  
35 oxygen bleaching agent in solution.

To solve the aforementioned temperature rate dependency, a class of compounds known as "bleach activators" has been developed. Bleach activators, typically perhydrolyzable acyl compounds having a leaving group such as oxybenzenesulfonate, react with the active oxygen group, typically hydrogen peroxide or its anion, to form a more effective peroxyacid oxidant. It is the peroxyacid compound which then oxidizes the stained or soiled substrate material. However, bleach activators are also somewhat temperature dependent. Bleach activators are more effective at warm water temperatures of from about 40 °C to about 60 °C. In water temperatures of less than about 40 °C, the peroxyacid compound loses some of its bleaching effectiveness.

Attempts have been made as disclosed in U.S. Patent Nos. 5,360,568, 5,360,569 and 5,370,826 all to Madison et al. to develop a bleach system which is effective in lower temperature water conditions. However, the cationic dihydroisoquinolinium bleach boosting compounds disclosed in these references, when combined with peroxygen compounds, undergo undesired decomposition, causing a reduction in organic catalyst compound efficiency.

U.S. Patent Nos. 5,576,282 and 5,817,614 both to Miracle et al. disclose a bleach system which is effective in lower temperature water conditions. The zwitterionic dihydroisoquinolinium, organic catalyst compounds, some of which are more or less resistant to decomposition by peroxygen compounds than the cationic dihydroisoquinolinium bleach boosting compounds above, do undergo undesired decomposition, causing a reduction in bleach booster compound efficiency.

Although these references disclose bleaching compositions comprising a bleach boosting compound (cationic dihydroisoquinolinium or zwitterionic dihydroisoquinolinium, which are distinctly different bleach boosting compounds) in the presence of a surfactant (anionic, nonionic, etc.), none of these references recognize or teach a problem with the stability of their respective bleach boosting compounds in the presence of a peroxygen compound, such as a peracid, nor do any of these references teach a synergistic effect between their respective bleach boosting compounds, especially the cationic bleach boosting compounds, and anionic surfactants.

In light of the foregoing, researchers have been trying to develop a bleach system that provides effective bleach boosting compounds, as well as other organic catalyst compounds, such as modified amine compounds, and compositions containing such bleach boosting compounds which provide effective bleaching in lower water temperatures and which exhibit increased stability and resist decomposition in the presence of a peroxygen compound. In other words, the researchers have been trying to develop organic catalyst compounds that exhibit a prolonged effective lifetime.

Accordingly, there remains a need for effective organic catalyst compounds and compositions containing organic catalyst compounds which provide effective bleaching even in lower water temperatures, and resist decomposition by peroxygen compounds.

#### Summary of the Invention

This need is met by the present invention wherein bleaching compositions comprising organic catalyst compounds such as bleach boosting compounds, specifically bleach boosters and/or bleaching species, modified amine compounds and/or modified amine oxide compounds, sulfonimines, phosphonimines, N-acylimines and/or thiodiazole dioxides in combination with an anionic surfactant are provided that perform effective bleaching at lower water temperatures.

It has been surprisingly found that the organic catalyst compounds of the present invention, especially the cationic bleach boosting compounds of the present invention, exhibit prolonged effective lifetimes (increased stability and resistance against decomposition in the presence of a peroxygen compound) in the presence of an anionic surfactant.

The combination of the organic catalyst compounds and the anionic surfactant resists or inhibits the decomposition of the organic catalyst compounds of the present invention.

In one aspect of the present invention, a bleaching composition comprising an organic catalyst compound, in conjunction with or without a peroxygen source, and an anionic surfactant is provided.

In accordance with another aspect of the present invention, a method for laundering a fabric in need of cleaning comprising contacting the fabric with a laundry solution having a bleaching composition in accordance with the present invention as described herein is provided.

In accordance with still yet another aspect of the present invention, a laundry additive product comprising an organic catalyst compound and an anionic surfactant is provided.

Accordingly, it is an object of the present invention to provide: a bleaching composition comprising an organic catalyst compound and an anionic surfactant, wherein the bleaching composition resists decomposition of the organic catalyst compound and effectively prolongs the effective life of the organic catalyst compound compared to a bleaching composition comprising an organic catalyst compound without an anionic surfactant; a bleaching composition comprising an organic catalyst compound and an anionic surfactant which demonstrates improved performance even in lower temperature solutions; a method for laundering a fabric by employing a bleaching composition comprising an organic catalyst compound and an anionic surfactant; and a laundry additive product containing an organic catalyst compound and an anionic surfactant. These, and other objects, features and advantages of the present invention will be recognized by one of ordinary skill in the art from the following description and the appended claims.

All percentages, ratios and proportions herein are on a weight basis unless otherwise indicated. All documents cited herein are hereby incorporated by reference.

#### Detailed Description of the Invention

5       The present invention discloses bleaching compositions comprising an organic catalyst compound, preferably branched organic catalyst compound, and an anionic surfactant which provide superior bleaching performance compared to bleaching compositions comprising an organic catalyst compound without an anionic surfactant.

10       The present invention further discloses bleaching compositions comprising an organic catalyst compound and an anionic surfactant which resist or inhibit the decomposition of the organic catalyst compound compared to bleaching compositions comprising an organic catalyst compound without an anionic surfactant. This resistance or inhibition to decompose results in the organic catalyst compounds having a prolonged effective life compared to organic catalyst compounds present in bleaching compositions without an anionic surfactant.

15       The bleaching compositions of the present invention provide increased bleaching effectiveness even in lower temperature applications while being resistant to unwanted decomposition by aromatization, resulting in longer lasting performance.

20       The organic catalyst compounds of the present invention act in conjunction with or without, preferably with conventional peroxygen bleaching sources to provide the above-mentioned increased bleaching effectiveness and superior resistance to aromatization.

#### DEFINITIONS

25       "Peroxygen source" as used herein means materials that generate peroxygen compounds, which can include the peroxygen compounds themselves. Examples include, but are not limited to, bleach activators, peracids, percarbonate, perborate, hydrogen peroxide, bleach boosting compounds, and/or bleaching species (e.g., oxaziridiniums).

      "Peroxygen compounds" as used herein includes peracids and peroxides (e.g., hydrogen peroxide, alkyl hydroperoxides, etc).

      "Peracid" as used herein means a peroxyacid such as peroxycarboxylic acid and/or peroxymonosulfuric acid (tradename OXONE) and their salts.

#### ORGANIC CATALYST COMPOUNDS

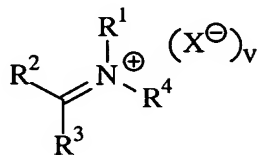
30       Nonlimiting examples of bleach boosting and bleaching species compounds are described in U.S. Patent Nos. 5,041,232, 5,045,223, 5,047,163, 5,310,925, 5,413,733, 5,360,568, 5,482,515, 5,550,256, 5,360,569, 5,478,357, 5,370,826, 5,442,066, 5,576,282, 5,760,222, 5,753,599 and 5,652,207, PCT Published Applications WO 98/23602, WO 95/13352, WO 95/13353, WO

95/13351, WO 97/06147 and WO 98/23717, EP 728 182, and pending, soon to be issued, U.S. Patent Application No. 08/697,743.

Preferably, the organic catalyst compounds of the present invention, more preferably iminium-based organic catalyst compounds, include, but are not limited to, bleach boosting compounds, bleaching species, modified amines, modified amine oxides, sulfonylimines, phosphonimines, N-acylimines, thiodiazole and mixtures thereof.

Bleach Boosting Compounds - The bleach boosting compounds, preferably iminium-based bleach boosting compounds, include, but are not limited to, aryliminium cations, aryliminium polyions having a net charge of from about +3 to about -3, and aryliminium zwitterions having a net charge of from about +3 to about -3.

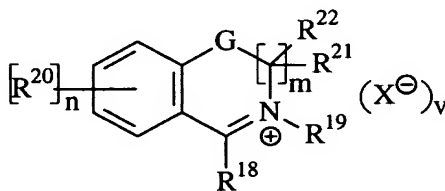
The aryliminium cations and aryliminium polyions having a net charge of from about +3 to about -3, are represented by the formula [I]:



[I]

where  $\text{R}^2$  and  $\text{R}^3$  are independently selected from substituted or unsubstituted radicals selected from the group consisting of H, alkyl, cycloalkyl, aryl, alkaryl, aralkyl, heterocyclic ring, silyl, nitro, halo, cyano, sulfonato, alkoxy, keto, carboxylic and carboalkoxy radicals;  $\text{R}^1$  and  $\text{R}^4$  are selected from substituted or unsubstituted, saturated or unsaturated radicals selected from the group consisting of H, alkyl, cycloalkyl, aryl, alkaryl, aralkyl, heterocyclic ring, silyl, nitro, halo, cyano, alkoxy, keto and carboalkoxy radicals;  $\text{X}^-$  is a suitable charge-balancing counterion, preferably a bleach compatible counterion;  $v$  is an integer from 1 - 3.

Preferably, the aryliminium cations and aryliminium polyions having a net charge of from about +3 to about -3, are represented by the formula [XI]:



[XI]

where m is 1 to 3 when G is present and m is 1 to 4 when G is not present; n is an integer from 0 to 4; and each R<sup>20</sup> is independently selected from a substituted or unsubstituted radical selected from the group consisting of H, alkyl, cycloalkyl, aryl, fused aryl, heterocyclic ring, fused heterocyclic ring, nitro, halo, cyano, sulfonato, alkoxy, keto, carboxylic and carboalkoxy radicals, and any two vicinal R<sup>20</sup> substituents may combine to form a fused aryl, fused carbocyclic or fused heterocyclic ring, provided that R<sup>20</sup> is not phenyl; and provided that when R<sup>19</sup> is isopropyl, R<sup>20</sup> is not COCH<sub>3</sub>; R<sup>18</sup> may be a substituted or unsubstituted radical selected from the group consisting of H, alkyl, cycloalkyl, alkaryl, aryl, aralkyl, heterocyclic ring, silyl, nitro, halo, cyano, sulfonato, alkoxy, keto, carboxylic and carboalkoxy radicals; R<sup>19</sup> may be a substituted or unsubstituted, saturated or unsaturated, radical selected from the group consisting of H, alkyl, cycloalkyl, alkaryl, aryl, aralkyl and heterocyclic ring, preferably R<sup>19</sup> is a non-linear radical selected from the group consisting of a substituted or branched radical selected from the group consisting of alkyl, cycloalkyl, alkaryl, aryl (provided that this aryl group is not phenyl), aralkyl and non-aromatic heterocyclic ring, provided that when R<sup>19</sup> is isopropyl R<sup>20</sup> is not ArCOCH<sub>3</sub>; G is selected from the group consisting of: (1) -O-; (2) -N(R<sup>23</sup>)-; and (3) -N(R<sup>23</sup>R<sup>24</sup>)-; R<sup>21</sup> - R<sup>24</sup> are substituted or unsubstituted radicals independently selected from the group consisting of H, oxygen, linear or branched C<sub>1</sub>-C<sub>12</sub> alkyls, alkylenes, alkoxy, aryls, alkaryls, aralkyls, cycloalkyls and heterocyclic rings; provided that any of R<sup>18</sup>, R<sup>19</sup>, R<sup>20</sup>, R<sup>21</sup> - R<sup>24</sup> may be joined together with any other of R<sup>18</sup>, R<sup>19</sup>, R<sup>20</sup>, R<sup>21</sup> - R<sup>24</sup> to form part of a common ring; any geminal R<sup>21</sup> - R<sup>22</sup> may combine to form a carbonyl; any vicinal R<sup>21</sup> - R<sup>24</sup> may join to form unsaturation; and wherein any one group of substituents R<sup>21</sup> - R<sup>24</sup> may combine to form a substituted or unsubstituted fused unsaturated moiety; X<sup>-</sup> is a suitable charge-balancing, preferably bleach-compatible counterion; v is an integer from 1 - 3.

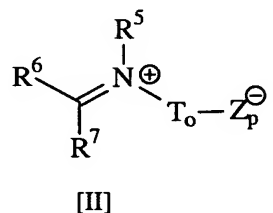
More preferred, aryliminium cations and aryliminium polyions having a net charge of from about +3 to about -3, as represented by the formula [XI], include those of formula [XI] where R<sup>18</sup> is H or methyl and R<sup>19</sup> is H or substituted or unsubstituted, saturated or unsaturated C<sub>1</sub> - C<sub>14</sub> alkyl and cycloalkyl.

Also preferably, R<sup>19</sup> and/or the ring carbon(s) containing the groups R<sup>21</sup> - R<sup>22</sup>, when present, include branching at one or more of the following positions, when present, alpha, beta, gamma, delta and epsilon positions, although branching may or may not also be present at other positions. Branch positions in accordance with the present invention as described here and hereinafter (i.e., alpha, beta, gamma, etc.) are defined in terms of position relative to the imine/iminium nitrogen atom of the organic catalyst compound for the nitrogen substituents R<sup>1</sup> and R<sup>4</sup> as represented by the formula [I].

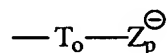
More preferably, R<sup>19</sup> and/or the ring carbon(s) containing the groups R<sup>21</sup> - R<sup>22</sup>, when present, include branching at one or more of the following positions, when present, beta, gamma, delta and epsilon positions, although branching may or may not also be present at the alpha position, as well as at other positions.

- 5 Even most preferably, R<sup>19</sup> and/or the ring carbon(s) containing the groups R<sup>21</sup> - R<sup>22</sup>, when present, include branching, when present, at the beta position, although branching may or may not also be present at the alpha, gamma, delta and epsilon positions, as well as at other positions.

- 10 The aryliminium zwitterions having a net charge of from about +3 to about -3, are represented by the formula [II]:

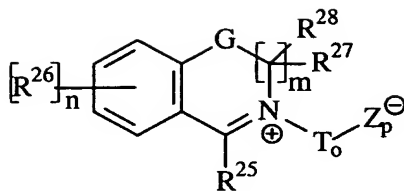


- 15 where R<sup>5</sup> - R<sup>7</sup> are independently selected from substituted or unsubstituted radicals selected from the group consisting of H, alkyl, cycloalkyl, aryl, alkaryl, aralkyl, heterocyclic ring, silyl, nitro, halo, cyano, sulfonato, alkoxy, keto, carboxylic and carboalkoxy radicals; the radical, preferably non-linear radical, represented by the formula:



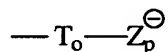
- 20 where Z<sub>p</sub><sup>-</sup> is covalently bonded to T<sub>o</sub>, and Z<sub>p</sub><sup>-</sup> is selected from the group consisting of -CO<sub>2</sub><sup>-</sup>, -SO<sub>3</sub><sup>-</sup>, -OSO<sub>3</sub><sup>-</sup>, -SO<sub>2</sub><sup>-</sup> and -OSO<sub>2</sub><sup>-</sup> and p is either 1, 2 or 3; T<sub>o</sub> is selected from the group consisting of substituted or unsubstituted, saturated or unsaturated alkyl, cycloalkyl, aryl, alkaryl, aralkyl and heterocyclic ring, preferably provided that when R<sup>6</sup> and R<sup>7</sup> are joined to R<sup>5</sup> by an
- 25 unsubstituted phenethyl group, the T<sub>o</sub> is not -(CH<sub>2</sub>)CHR<sup>T</sup> wherein R<sup>T</sup> is not H.

Preferably, the aryliminium zwitterions having a net charge of from about +3 to about -3 are represented by the formula [XII]:

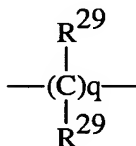


[XII]

where m is 1 to 3 when G is present and m is 1 to 4 when G is not present; n is an integer from 0 to 4; and each R<sup>26</sup> is independently selected from a substituted or unsubstituted radical selected from the group consisting of H, alkyl, cycloalkyl, aryl, fused aryl, heterocyclic ring, fused heterocyclic ring, nitro, halo, cyano, sulfonato, alkoxy, keto, carboxylic and carboalkoxy radicals, and any two vicinal R<sup>26</sup> substituents may combine to form a fused aryl, fused carbocyclic or fused heterocyclic ring; R<sup>25</sup> may be a substituted or unsubstituted radical selected from the group consisting of H, alkyl, cycloalkyl, alkaryl, aryl, aralkyl, heterocyclic ring, silyl, nitro, halo, cyano, sulfonato, alkoxy, keto, carboxylic and carboalkoxy radicals; also present in this formula is the radical, preferably non-linear radical, represented by the formula:



where Z<sub>p</sub><sup>-</sup> is covalently bonded to T<sub>o</sub>, and Z<sub>p</sub><sup>-</sup> is selected from the group consisting of -CO<sub>2</sub><sup>-</sup>, -SO<sub>3</sub><sup>-</sup>, -OSO<sub>3</sub><sup>-</sup>, -SO<sub>2</sub><sup>-</sup> and -OSO<sub>2</sub><sup>-</sup> and p is either 1, 2 or 3; T<sub>o</sub> is selected from the group consisting of:

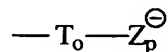


wherein q is an integer from 1 to 8; R<sup>29</sup> is independently selected from substituted or unsubstituted radicals selected from the group consisting of linear or branched H, alkyl, cycloalkyl, alkaryl, aryl, aralkyl, alkylene, heterocyclic ring, alkoxy, arylcarbonyl, carboxyalkyl and amide groups; G is selected from the group consisting of: (1) -O-; (2) -N(R<sup>30</sup>)-; and (3) -N(R<sup>30</sup>R<sup>31</sup>)-; R<sup>27</sup>, R<sup>28</sup>, R<sup>30</sup> and R<sup>31</sup> are substituted or unsubstituted radicals independently selected from the group consisting of H, oxygen, alkyl, cycloalkyl, alkaryl, aryl, aralkyl, alkenes, heterocyclic ring, alkoxys, arylcarbonyl groups, carboxyalkyl groups and amide groups; any of R<sup>25</sup>, R<sup>26</sup>, R<sup>27</sup>, R<sup>28</sup>, R<sup>30</sup> and R<sup>31</sup> may be joined together with any other of R<sup>25</sup>, R<sup>26</sup>, R<sup>27</sup>, R<sup>28</sup>, R<sup>30</sup> and R<sup>31</sup> to form part of a common ring; any geminal R<sup>27</sup> - R<sup>28</sup> may combine to



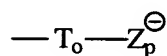
form a carbonyl; any vicinal R<sup>27</sup> - R<sup>31</sup> may join to form unsaturation; and wherein any one group of substituents R<sup>27</sup> - R<sup>31</sup> may combine to form a substituted or unsubstituted fused unsaturated moiety.

- 5 More preferred aryliminium zwitterions having a net charge of from about +3 to about -3, as represented by the formula [XII], include those of formula [XII] where R<sup>25</sup> is H or methyl, and for the radical, preferably non-linear radical, represented by the formula:



- 10 Z<sub>p</sub><sup>-</sup> is -CO<sub>2</sub><sup>-</sup>, -SO<sub>3</sub><sup>-</sup> or -OSO<sub>3</sub><sup>-</sup>, and p is 1.

Also preferably,



- 15 and/or the ring carbon(s) containing the groups R<sup>27</sup> - R<sup>28</sup>, when present, include branching at one or more of the following positions, when present, alpha, beta, gamma, delta and epsilon positions, although branching may or may not also be present at other positions.

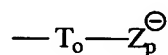
More preferably,

- 20  $-T_o-Z_p^{\ominus}$

- and/or the ring carbon(s) containing the groups R<sup>27</sup> - R<sup>28</sup>, when present, include branching at one or more of the following positions, when present, beta, gamma, delta and epsilon positions, although branching may or may not also be present at the alpha position, as well as at other positions.

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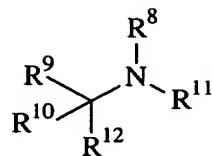
Even more preferably,



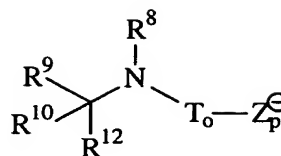
- 30 and/or the ring carbon(s) containing the groups R<sup>27</sup> - R<sup>28</sup>, when present, includes branching, when present, at the beta position, although branching may or may not also be present at the alpha, gamma, delta and epsilon positions, as well as at other positions.

- Modified Amine Compounds - The modified amine compounds of the present invention include, but are not limited to, modified amines and modified amine oxides having a net charge of
- 35 from about +3 to about -3.

The modified amine oxides are represented by formulas [V] and [VI]:

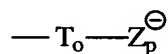


[V]



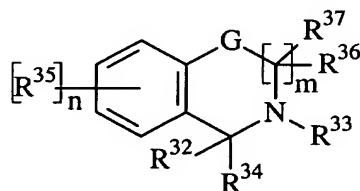
[VI]

- 5 where  $R^9$  and  $R^{10}$  are independently selected from substituted or unsubstituted radicals selected from the group consisting of H, alkyl, cycloalkyl, aryl, alkaryl, aralkyl, heterocyclic ring, silyl, nitro, halo, cyano, sulfonato, alkoxy, keto, carboxylic and carboalkoxy radicals and anionic and/or cationic charge carrying radicals;  $R^8$  and  $R^{11}$ , preferably non-linear radicals, are selected from the group consisting of substituted or branched alkyl, cycloalkyl, aryl, alkaryl, aralkyl, heterocyclic ring, silyl, nitro, halo, cyano, alkoxy, keto and carboalkoxy radicals and anionic and/or cationic charge carrying radicals;  $R^{12}$  is a leaving group, the protonated form of which has a  $pK_a$  value (H<sub>2</sub>O reference) that falls within the following range:  $37 > pK_a > -2$ ; with the proviso that any  $R^8$  -  $R^{12}$ , when present, may combine to form a fused aryl, fused carbocyclic or fused heterocyclic ring; and the radical, preferably non-linear radical, represented by the formula:

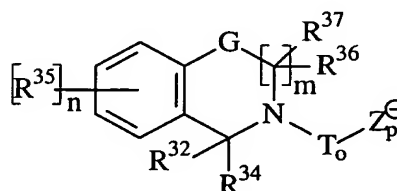


- 15 where  $Z_p^+$  is covalently bonded to  $T_o$ , and  $Z_p^+$  is selected from the group consisting of  $-CO_2^+$ ,  $-SO_3^+$ ,  $-OSO_3^+$ ,  $-SO_2^+$  and  $-OSO_2^+$  and  $p$  is either 1, 2 or 3;  $T_o$  is selected from the group consisting of substituted or unsubstituted, saturated or unsaturated alkyl, cycloalkyl, aryl, alkaryl, aralkyl and heterocyclic ring.

20 Preferably, the modified amines are represented by the formulas [XV] and [XVI]:



[XV]

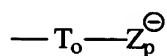


[XVI]

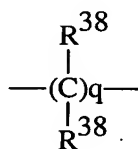
25 where  $m$  is 1 to 3 when  $G$  is present and  $m$  is 1 to 4 when  $G$  is not present;  $n$  is an integer from 0 to 4; and  $R^{34}$  is a radical selected from the group consisting of substituted or unsubstituted,

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5 saturated or unsaturated hydroxy, perhydroxy, alkoxy, peralkoxy, carboxylic, percarboxylic, sulfonato, and persulfonato radicals; each  $R^{35}$  is independently selected from a substituted or unsubstituted radical selected from the group consisting of H, alkyl, cycloalkyl, aryl, fused aryl, heterocyclic ring, fused heterocyclic ring, nitro, halo, cyano, sulfonato, alkoxy, keto, carboxylic and carboalkoxy radicals, and any two vicinal  $R^{35}$  substituents may combine to form a fused aryl, fused carbocyclic or fused heterocyclic ring;  $R^{32}$  may be a substituted or unsubstituted radical selected from the group consisting of H, alkyl, cycloalkyl, alkaryl, aryl, aralkyl, heterocyclic ring, silyl, nitro, halo, cyano, sulfonato, alkoxy, keto, carboxylic, and carboalkoxy radicals;  $R^{33}$  may be a substituted or unsubstituted, saturated or unsaturated, radical selected from the group consisting of substituted or unsubstituted H, alkyl, cycloalkyl, alkaryl, aryl, aralkyl and heterocyclic ring, preferably a non-linear radical; also present in this formula is a radical, preferably non-linear radical, represented by the formula:



15 where  $Z_p^-$  is covalently bonded to  $T_o$ , and  $Z_p^-$  is selected from the group consisting of  $-CO_2^-$ ,  $-SO_3^-$ ,  $-OSO_3^-$ ,  $-SO_2^-$  and  $-OSO_2^-$ , and p is either 1, 2 or 3;  $T_o$  is selected from the group consisting of:



20 wherein q is an integer from 1 to 8;  $R^{38}$  is independently selected from substituted or unsubstituted radicals selected from the group consisting of linear or branched H, alkyl, cycloalkyl, alkaryl, aryl, aralkyl, alkylene, heterocyclic ring, alkoxy, arylcarbonyl, carboxyalkyl and amide groups, provided that all  $R^{38}$  groups are not independently selected to be H; G is selected from the group consisting of: (1) -O-; (2) -N( $R^{39}$ )-; and (3) -N( $R^{39}R^{40}$ )-;  $R^{36}$ ,  $R^{37}$ ,  $R^{39}$  and  $R^{40}$  are substituted or unsubstituted radicals independently selected from the group consisting of H, oxygen, alkyl, cycloalkyl, alkaryl, aryl, aralkyl, alkylenes, heterocyclic ring, alkoxy, arylcarbonyl groups, carboxyalkyl groups and amide groups; any of  $R^{32}$ ,  $R^{33}$ ,  $R^{34}$ ,  $R^{35}$ ,  $R^{36}$ ,  $R^{37}$ ,  $R^{39}$  and  $R^{40}$  may be joined together with any other of  $R^{32}$ ,  $R^{33}$ ,  $R^{34}$ ,  $R^{35}$ ,  $R^{36}$ ,  $R^{37}$ ,  $R^{39}$  and  $R^{40}$  to form part of a common ring; any geminal  $R^{36}$ - $R^{37}$  may combine to form a carbonyl; any vicinal  $R^{36}$ ,  $R^{37}$ ,  $R^{39}$  and  $R^{40}$  may join to form unsaturation; and wherein any one group of substituents  $R^{36}$ ,  $R^{37}$ ,  $R^{39}$  and  $R^{40}$  may combine to form a substituted or unsubstituted fused unsaturated moiety.

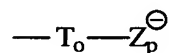
Preferably, R<sup>33</sup> and/or the ring carbon(s) containing the groups R<sup>36</sup> - R<sup>37</sup>, when present, include branching at one or more of the following positions, when present, alpha, beta, gamma, delta and epsilon positions, although branching may or may not also be present at other positions.

5 More preferably, R<sup>33</sup> and/or the ring carbon(s) containing the groups R<sup>36</sup> - R<sup>37</sup>, when present, include branching at one or more of the following positions, when present, beta, gamma, delta and epsilon positions, although branching may or may not also be present at the alpha position, as well as at other positions.

10 Even most preferably, R<sup>33</sup> and/or the ring carbon(s) containing the groups R<sup>36</sup> - R<sup>37</sup>, when present, include branching, when present, at the beta position, although branching may or may not also be present at the alpha, gamma, delta and epsilon positions, as well as at other positions.

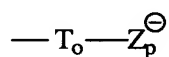
Preferably, modified amines, as represented by the formulas [XV] and [XVI], include those modified amines having a net charge of about +1 to about -1 where R<sup>32</sup> is H or methyl, and Z<sub>p</sub><sup>-</sup> is -CO<sub>2</sub><sup>-</sup>, -SO<sub>3</sub><sup>-</sup> or -OSO<sub>3</sub><sup>-</sup>.

15 Also preferably,



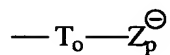
20 and/or the ring carbon(s) containing the groups R<sup>36</sup> - R<sup>37</sup>, when present, include branching at one or more of the following positions, when present, alpha, beta, gamma, delta and epsilon positions, although branching may or may not also be present at other positions.

More preferably,



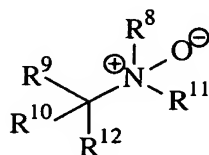
25 and/or the ring carbon(s) containing the groups R<sup>36</sup> - R<sup>37</sup>, when present, include branching at one or more of the following positions, when present, beta, gamma, delta and epsilon positions, although branching may or may not also be present at the alpha position, as well as at other positions.

30 Even more preferably,

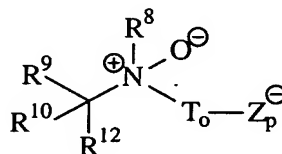


35 and/or the ring carbon(s) containing the groups R<sup>36</sup> - R<sup>37</sup>, when present, includes branching, when present, at the beta position, although branching may or may not also be present at the alpha, gamma, delta and epsilon positions, as well as at other positions.

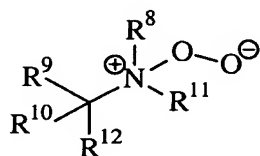
The modified amine oxides of the present invention are represented by formulas [VII]-[X]:



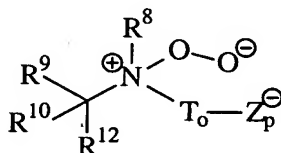
[VII]



[VIII]

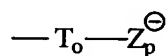


[IX]



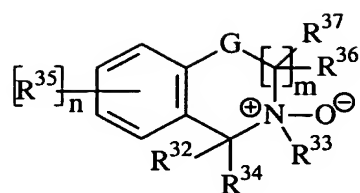
[X]

- where  $\text{R}^9$  and  $\text{R}^{10}$  are independently selected from substituted or unsubstituted radicals selected from the group consisting of H, alkyl, cycloalkyl, aryl, alkaryl, aralkyl, heterocyclic ring, silyl, nitro, halo, cyano, sulfonato, alkoxy, keto, carboxylic and carboalkoxy radicals and anionic and/or cationic charge carrying radicals;  $\text{R}^8$  and  $\text{R}^{11}$  are radicals, at least one of which is preferably a non-linear radical, selected from the group consisting of substituted or unsubstituted alkyl, cycloalkyl, aryl, alkaryl, aralkyl, heterocyclic ring, silyl, nitro, halo, cyano, alkoxy, keto and carboalkoxy radicals and anionic and/or cationic charge carrying radicals;  $\text{R}^{12}$  is a leaving group, the protonated form of which has a  $\text{pK}_a$  value ( $\text{H}_2\text{O}$  reference) that falls within the following range:  $37 > \text{pK}_a > -2$ ; with the proviso that any  $\text{R}^8\text{-R}^{12}$ , when present, may combine to form a fused aryl, fused carbocyclic or fused heterocyclic ring; also present in the formula is the radical, preferably non-linear radical, represented by the formula:

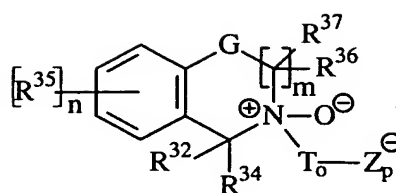


- where  $\text{Z}_p^-$  is covalently bonded to  $\text{T}_o$ , and  $\text{Z}_p^-$  is selected from the group consisting of  $-\text{CO}_2^-$ ,  $-\text{SO}_3^-$ ,  $-\text{OSO}_3^-$ ,  $-\text{SO}_2^-$  and  $-\text{OSO}_2^-$  and  $p$  is either 1, 2 or 3;  $\text{T}_o$  is selected from the group consisting of substituted or unsubstituted, saturated or unsaturated alkyl, cycloalkyl, aryl, alkaryl, aralkyl and heterocyclic ring.

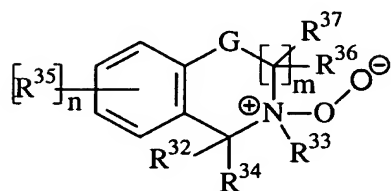
Preferably, the modified amine oxides are represented by formulas [XVII]-[XX]:



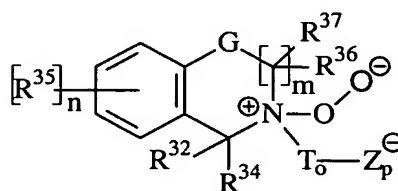
[XVII]



[XVIII]

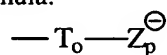


[XIX]

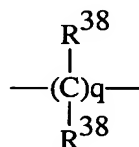


[XX]

where m is 1 to 3 when G is present and m is 1 to 4 when G is not present; n is an integer from 0 to 4; and R<sup>34</sup> is a radical selected from the group consisting of substituted or unsubstituted, saturated or unsaturated hydroxy, perhydroxy, alkoxy and peralkoxy radicals; each R<sup>35</sup> is independently selected from a substituted or unsubstituted radical selected from the group consisting of H, alkyl, cycloalkyl, aryl, fused aryl, heterocyclic ring, fused heterocyclic ring, nitro, halo, cyano, sulfonato, alkoxy, keto, carboxylic, and carboalkoxy radicals, and any two vicinal R<sup>35</sup> substituents may combine to form a fused aryl, fused carbocyclic or fused heterocyclic ring; R<sup>32</sup> may be a substituted or unsubstituted radical selected from the group consisting of H, alkyl, cycloalkyl, alkaryl, aryl, aralkyl, heterocyclic ring, silyl; nitro, halo, cyano, sulfonato, alkoxy, keto, carboxylic, and carboalkoxy radicals; R<sup>33</sup> is a radical selected from the group consisting of substituted or unsubstituted, saturated or unsaturated H, alkyl, cycloalkyl, alkaryl, aryl, aralkyl and heterocyclic ring, preferably non-linear radical; also present in this formula is a radical, preferably non-linear radical, represented by the formula:



where  $Z_p^-$  is covalently bonded to  $T_o$ , and  $Z_p^-$  is selected from the group consisting of  $-CO_2^-$ ,  $-SO_3^-$ ,  $-OSO_3^-$ ,  $-SO_2^-$  and  $-OSO_2^-$ , and p is either 1 or 2;  $T_o$  is selected from the group consisting of:



wherein q is an integer from 1 to 8; R<sup>38</sup> is independently selected from substituted or unsubstituted radicals selected from the group consisting of linear or branched H, alkyl, cycloalkyl, alkaryl, aryl, aralkyl, alkylene, heterocyclic ring, alkoxy, arylcarbonyl, carboxyalkyl and amide groups, provided that all R<sup>38</sup> groups are not independently selected to be H; G is selected from the group consisting of: (1) -O-; (2) -N(R<sup>39</sup>)-; and (3) -N(R<sup>39</sup>R<sup>40</sup>)-; R<sup>36</sup>, R<sup>37</sup>, R<sup>39</sup> and R<sup>40</sup> are substituted or unsubstituted radicals independently selected from the group consisting of H, oxygen, alkyl, cycloalkyl, alkaryl, aryl, aralkyl, alkenes, heterocyclic ring, alkoxy, arylcarbonyl groups, carboxyalkyl groups and amide groups; any of R<sup>32</sup>, R<sup>33</sup>, R<sup>34</sup>, R<sup>35</sup>, R<sup>36</sup>, R<sup>37</sup>, R<sup>39</sup> and R<sup>40</sup> may be joined together with any other of R<sup>32</sup>, R<sup>33</sup>, R<sup>34</sup>, R<sup>35</sup>, R<sup>36</sup>, R<sup>37</sup>, R<sup>39</sup> and R<sup>40</sup> to form part of a common ring; any geminal R<sup>36</sup>-R<sup>37</sup> may combine to form a carbonyl; any vicinal R<sup>36</sup>, R<sup>37</sup>, R<sup>39</sup> and R<sup>40</sup> may join to form unsaturation; and wherein any one group of substituents R<sup>36</sup>, R<sup>37</sup>, R<sup>39</sup> and R<sup>40</sup> may combine to form a substituted or unsubstituted fused unsaturated moiety.

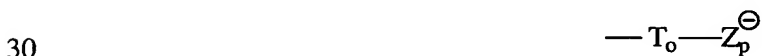
Preferably, R<sup>33</sup> and/or the ring carbon(s) containing the groups R<sup>36</sup> - R<sup>37</sup>, when present, include branching at one or more of the following positions, when present, alpha, beta, gamma, delta and epsilon positions, although branching may or may not also be present at other positions.

More preferably, R<sup>33</sup> and/or the ring carbon(s) containing the groups R<sup>36</sup> - R<sup>37</sup>, when present, include branching at one or more of the following positions, when present, beta, gamma, delta and epsilon positions, although branching may or may not also be present at the alpha position, as well as at other positions.

Even most preferably, R<sup>33</sup> and/or the ring carbon(s) containing the groups R<sup>36</sup> - R<sup>37</sup>, when present, include branching, when present, at the beta position, although branching may or may not also be present at the alpha, gamma, delta and epsilon positions, as well as at other positions.

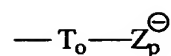
Preferably, modified amines, as represented by the formulas [XVII]-[XX], include those modified amines having a net charge of about +1 to about -1 where R<sup>32</sup> is H and/or Z<sub>p</sub><sup>-</sup> is -CO<sub>2</sub><sup>-</sup>, -SO<sub>3</sub><sup>-</sup>, or -OSO<sub>3</sub><sup>-</sup>, even more preferably Z<sub>p</sub><sup>-</sup> is -SO<sub>3</sub><sup>-</sup> or -OSO<sub>3</sub><sup>-</sup>.

Also preferably,



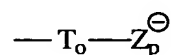
and/or the ring carbon(s) containing the groups R<sup>36</sup> - R<sup>37</sup>, when present, include branching at one or more of the following positions, when present, alpha, beta, gamma, delta and epsilon positions, although branching may or may not also be present at other positions.

More preferably,



and/or the ring carbon(s) containing the groups  $R^{36}$  -  $R^{37}$ , when present, include branching at one or more of the following positions, when present, beta, gamma, delta and epsilon positions, although branching may or may not also be present at the alpha position, as well as at other positions.

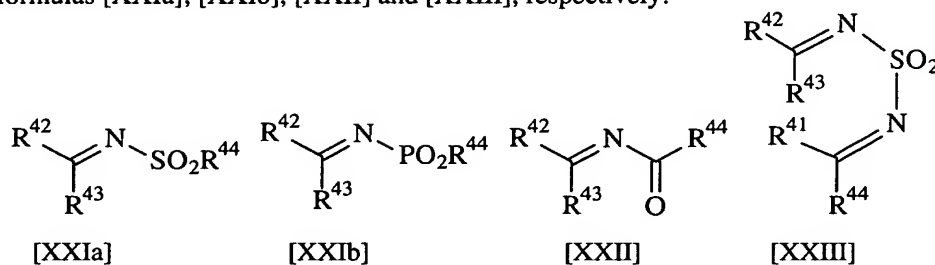
Even more preferably,



and/or the ring carbon(s) containing the groups  $R^{36}$  -  $R^{37}$ , when present, includes branching, when present, at the beta position, although branching may or may not also be present at the alpha, gamma, delta and epsilon positions, as well as at other positions.

For the modified amine compounds,  $R^{12}$  is a leaving group (LG), the protonated form of which has a  $pK_a$  value ( $H_2O$  reference) that fall within the following range:  $37 > pK_a > -2$ ; preferably  $30 > pK_a > 0$ ; more preferably  $23 > pK_a > 3$ ; even more preferably  $17 > pK_a > 11$ ; most preferably  $R^{12}$  is a leaving group consisting of substituted or unsubstituted, saturated or unsaturated hydroxy, perhydroxy, alkoxy and peralkoxy radicals, and any  $R^8$ - $R^{12}$  may combine to form a fused aryl, fused carbocyclic or fused heterocyclic ring.

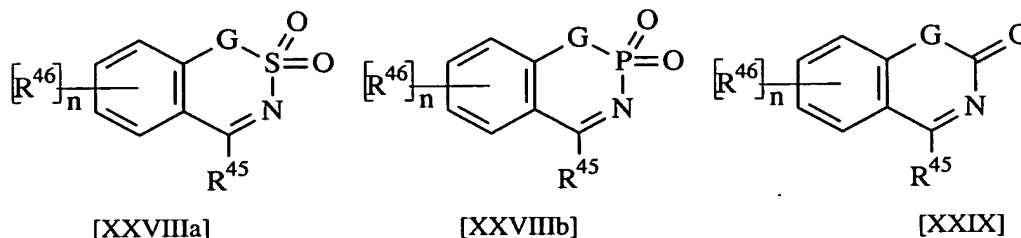
Sulfonimines, Phosphonimines, N-Acylamines, Thiodiazole Dioxides - The sulfonimines, phosphonimines, N-acylimines and thiodiazole dioxides of the present invention are represented by the formulas [XXIa], [XXIb], [XXII] and [XXIII], respectively:



where  $R^{41}$ - $R^{44}$ , when present, are independently selected from substituted or unsubstituted, saturated or unsaturated radicals selected from the group consisting of H, alkyl, cycloalkyl, aryl, alkaryl, aralkyl, heterocyclic ring, silyl, nitro, halo, cyano, sulfonato, alkoxy, keto, carboxylic and carboalkoxy radicals; provided that any of  $R^{41}$ - $R^{44}$  may be joined together with any other  $R^{41}$ - $R^{44}$  to form part of a common ring, including a fused aryl, fused carbocyclic or fused heterocyclic ring.



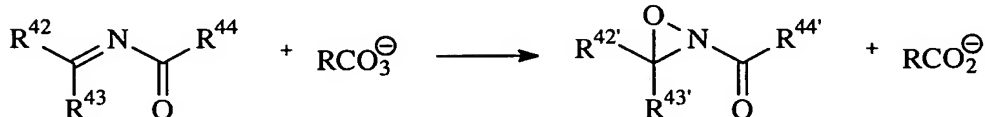
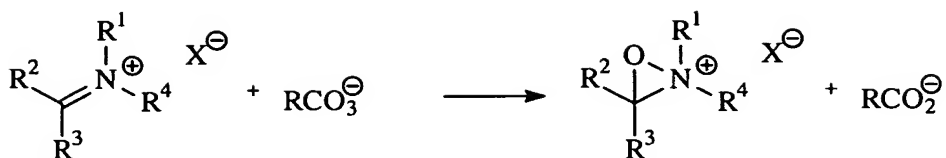
Preferably, the sulfonimines [XXVIIIa], phosphonimines [XXVIIIb], N-acylimines [XXIX] are represented as follows:



wherein n is an integer from 0 to 4; each  $R^{46}$  is independently selected from a substituted or unsubstituted radical selected from the group consisting of H, alkyl, cycloalkyl, aryl, fused aryl, heterocyclic ring, fused heterocyclic ring, nitro, halo, cyano, sulfonato, alkoxy, keto, carboxylic, and carboalkoxy radicals, and any two vicinal  $R^{46}$  substituents may combine to form a fused aryl, fused carbocyclic or fused heterocyclic ring;  $R^{45}$  may be a substituted or unsubstituted radical selected from the group consisting of H, alkyl, cycloalkyl, alkaryl, aryl, aralkyl, heterocyclic ring, silyl, nitro, halo, cyano, sulfonato, alkoxy, keto, carboxylic, and carboalkoxy radicals; G, when present, is selected from the group consisting of: (1) -O-; (2) -N( $R^{47}$ )-; and (3) -N( $R^{47}R^{48}$ )-;  $R^{47}$ - $R^{48}$  are substituted or unsubstituted radicals independently selected from the group consisting of H, oxygen, linear or branched  $C_1$ - $C_{12}$  alkyls, alkylenes, alkoxys, aryls, alkaryls, aralkyls, cycloalkyls, and heterocyclic rings.

**II. Bleaching Species** - The bleaching species (oxaziridiniums, oxaziridines) may also be used directly in accordance with the present invention. The bleaching species of the present invention include, but are not limited to, oxaziridinium cations, oxaziridinium polyions, which have a net charge of from about +3 to about -3, oxaziridinium zwitterions, which have a net charge of from about +3 to about -3, oxaziridine sulfonimines, oxaziridine phosphonimines, oxaziridine thiodiazole dioxides, and mixtures thereof.

The organic catalysts, especially the aryliminium cations, aryliminium polyions, aryliminium zwitterions, sulfonimines, phosphonimines, thiodiazole dioxides of the present invention act in conjunction with a peroxygen source, when present to increase bleaching effectiveness. Without being bound by theory, it is believed that the organic catalysts react with the peroxygen source to form a more active bleaching species, a quaternary oxaziridinium and/or oxaziridine compounds, as represented by the following reaction by way of example:

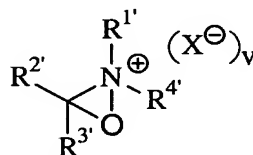


5

The oxaziridinium and/or oxaziridine compounds can have an increased or preferred activity at lower temperatures relative to the peroxygen compound.

a. Oxaziridinium Cations and Polyions - The oxaziridinium cations and polyions, which have a net charge of from about +3 to about -3, are represented by the formula [III]:

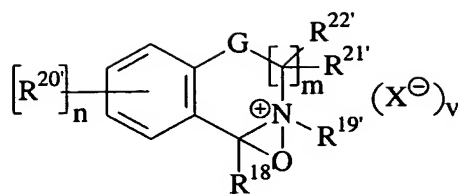
10



[III]

where R<sup>2'</sup> and R<sup>3'</sup> are independently selected from substituted or unsubstituted radicals selected from the group consisting of H, alkyl, cycloalkyl, aryl, alkaryl, aralkyl, heterocyclic ring, silyl, nitro, halo, cyano, sulfonato, alkoxy, keto, carboxylic and carboalkoxy radicals; R<sup>1'</sup> and R<sup>4'</sup> are radicals selected from the group consisting of substituted or unsubstituted, saturated or unsaturated, H alkyl, cycloalkyl, aryl, alkaryl, aralkyl, heterocyclic ring, silyl, nitro, halo, cyano, alkoxy, keto and carboalkoxy radicals; and v is an integer from 1 to 3.

Preferably, the oxaziridinium cations and polyions having a net charge of from about +3 to about -3, are represented by formula [XIII]:



[XIII]

- 5 wherein m is 1 to 3 when G is present and m is 1 to 4 when G is not present; n is an integer from 0 to 4; and each  $R^{20'}$  is independently selected from a substituted or unsubstituted radical selected from the group consisting of H, alkyl, cycloalkyl, aryl, fused aryl, heterocyclic ring, fused heterocyclic ring, nitro, halo, cyano, sulfonato, alkoxy, keto, carboxylic, and carboalkoxy radicals, and any two vicinal  $R^{20'}$  substituents may combine to form a fused aryl, fused carbocyclic or
- 10 fused heterocyclic ring;  $R^{18'}$  may be a substituted or unsubstituted radical selected from the group consisting of H, alkyl, cycloalkyl, alkaryl, aryl, aralkyl, heterocyclic ring, silyl, nitro, halo, cyano, sulfonato, alkoxy, keto, carboxylic, and carboalkoxy radicals;  $R^{19'}$  may be a substituted or unsubstituted, saturated or unsaturated, radical selected from the group consisting of H, alkyl, cycloalkyl, alkaryl, aryl, aralkyl and heterocyclic ring, preferably  $R^{19'}$  is a non-linear radical
- 15 selected from the group consisting of a substituted or branched radical selected from the group consisting of alkyl, cycloalkyl, alkaryl, aryl (provided that this aryl group is not phenyl), aralkyl and non-aromatic heterocyclic ring; G is selected from the group consisting of: (1) -O-; (2) -N( $R^{23'}$ )-; and (3) -N( $R^{23'}R^{24'}$ )-;  $R^{21'}$ - $R^{24'}$  are substituted or unsubstituted radicals independently selected from the group consisting of H, oxygen, linear or branched  $C_1 - C_{12}$
- 20 alkyls, alkylenes, alkoxy, aryls, alkaryls, aralkyls, cycloalkyls and heterocyclic rings; provided that any of  $R^{18'}$ ,  $R^{19'}$ ,  $R^{21'}$  -  $R^{24'}$  may be joined together with any other of  $R^{18'}$ ,  $R^{19'}$ ,  $R^{21'}$  -  $R^{24'}$  to form part of a common ring; any geminal  $R^{21'}$  -  $R^{22'}$  may combine to form a carbonyl; any vicinal  $R^{21'}$  -  $R^{24'}$  may join to form unsaturation; and wherein any one group of substituents  $R^{21'}$  -  $R^{24'}$  may combine to form a substituted or unsubstituted fused unsaturated moiety; and
- 25 wherein any one group of substituents  $R^{21'}$  -  $R^{24'}$  may combine to form a substituted or unsubstituted fused unsaturated moiety;  $X^-$  is a suitable charge-balancing, preferably bleach-compatible counterion; v is an integer from 1 to 3;

Preferred oxaziridinium cations and oxaziridinium polyions having a net charge of from about +3 to about -3, as represented by the formula [XIII], include those of formula [XIII] where

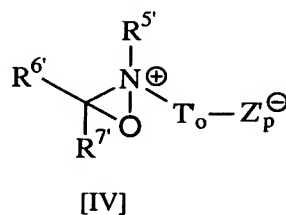
30  $R^{18'}$  is H or methyl, and  $R^{19'}$  is selected from the group consisting of H and linear or branched  $C_1$ - $C_{18}$  substituted or unsubstituted alkyl and cycloalkyl, more preferably where  $R^{19'}$  is substituted or branched  $C_3 - C_{14}$  alkyl and cycloalkyl.

Also preferably,  $R^{19'}$  and/or the ring carbon(s) containing the groups  $R^{21'}$  -  $R^{22'}$ , when present, include branching at one or more of the following positions, when present, alpha, beta, gamma, delta and epsilon positions, although branching may or may not also be present at other positions.

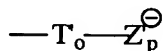
5 More preferably,  $R^{19'}$  and/or the ring carbon(s) containing the groups  $R^{21'}$  -  $R^{22'}$ , when present, include branching at one or more of the following positions, when present, beta, gamma, delta and epsilon positions, although branching may or may not also be present at the alpha position, as well as at other positions.

10 Even most preferably,  $R^{19'}$  and/or the ring carbon(s) containing the groups  $R^{21'}$  -  $R^{22'}$ , when present, include branching, when present, at the beta position, although branching may or may not also be present at the alpha, gamma, delta and epsilon positions, as well as at other positions.

b. Oxaziridinium Zwitterions - The oxaziridinium zwitterions, which have a net charge of from about +3 to about -3, are represented by formula [IV]:

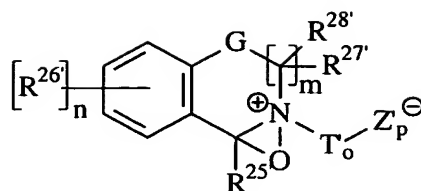


20 where  $R^{5'}$  -  $R^{7'}$  are independently selected from substituted or unsubstituted radicals selected from the group consisting of H, alkyl, cycloalkyl, aryl, alkaryl, aralkyl, heterocyclic ring, silyl, nitro, halo, cyano, sulfonato, alkoxy, keto, carboxylic and carboalkoxy radicals; also present in this formula is the radical, preferably non-linear radical, represented by the formula:



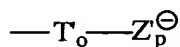
where  $Z_p^-$  is covalently bonded to  $T_o$ , and  $Z_p^-$  is selected from the group consisting of  $-CO_2^-$ ,  $-SO_3^-$ ,  $-OSO_3^-$ ,  $-SO_2^-$  and  $-OSO_2^-$  and p is either 1, 2 or 3;  $T_o$  is selected from the group consisting of substituted or unsubstituted, saturated or unsaturated alkyl, cycloalkyl, aryl, alkaryl, aralkyl and heterocyclic ring.

30 Preferably, the oxaziridinium zwitterions having a net charge of from about +3 to about -3, and are represented by formula [XIV]:

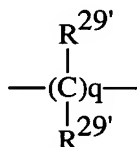


[XIV]

- wherein m is 1 to 3 when G is present and m is 1 to 4 when G is not present; n is an integer from 0 to 4; and each R<sup>26'</sup> is independently selected from a substituted or unsubstituted radical selected from the group consisting of H, alkyl, cycloalkyl, aryl, fused aryl, heterocyclic ring, fused heterocyclic ring, nitro, halo, cyano, sulfonato, alkoxy, keto, carboxylic, and carboalkoxy radicals, and any two vicinal R<sup>26'</sup> substituents may combine to form a fused aryl, fused carbocyclic or fused heterocyclic ring; R<sup>25'</sup> may be a substituted or unsubstituted radical selected from the group consisting of H, alkyl, cycloalkyl, alkaryl, aryl, aralkyl, heterocyclic ring, silyl, nitro, halo, cyano, sulfonato, alkoxy, keto, carboxylic, and carboalkoxy radicals; also present in this formula is the radical, preferably non-linear radical, represented by the formula:



- where Z<sub>p</sub><sup>-</sup> is covalently bonded to T<sub>o</sub>, and Z<sub>p</sub><sup>-</sup> is selected from the group consisting of -CO<sub>2</sub><sup>-</sup>, -SO<sub>3</sub><sup>-</sup>, -OSO<sub>3</sub><sup>-</sup>, -SO<sub>2</sub><sup>-</sup> and -OSO<sub>2</sub><sup>-</sup>, and p is either 1, 2 or 3; T<sub>o</sub> is selected from the group consisting of:



- wherein q is an integer from 1 to 8; R<sup>29'</sup> is independently selected from substituted or unsubstituted radicals selected from the group consisting of linear or branched H, alkyl, cycloalkyl, alkaryl, aryl, aralkyl, alkylene, heterocyclic ring, alkoxy, arylcarbonyl, carboxyalkyl and amide groups, provided that all R<sup>29'</sup> groups are not independently selected to be H; G is selected from the group consisting of: (1) -O-; (2) -N(R<sup>30'</sup>)-; and (3) -N(R<sup>30'</sup>R<sup>31'</sup>)-; R<sup>27'</sup>, R<sup>28'</sup>, R<sup>30'</sup> and R<sup>31'</sup> are substituted or unsubstituted radicals independently selected from the group consisting of H, oxygen, alkyl, cycloalkyl, alkaryl, aryl, aralkyl, alkylenes, heterocyclic ring, alkoxys, arylcarbonyl groups, carboxyalkyl groups and amide groups; any of R<sup>25'</sup>, R<sup>26'</sup>, R<sup>27'</sup>, R<sup>28'</sup>, R<sup>30'</sup> and R<sup>31'</sup> may be joined together with any other of R<sup>25'</sup>, R<sup>26'</sup>, R<sup>27'</sup>, R<sup>28'</sup>, R<sup>30'</sup> and R<sup>31'</sup> to form part of a common ring; any geminal R<sup>27'</sup> - R<sup>28'</sup> may combine to form a carbonyl;

any vicinal R<sup>27'</sup> - R<sup>31'</sup> may join to form unsaturation; and wherein any one group of substituents R<sup>27'</sup> - R<sup>31'</sup> may combine to form a substituted or unsubstituted fused unsaturated moiety, preferably provided that the radical represented by the formula:

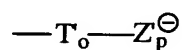


is a non-linear radical; and further provided that the radical represented by the formula:



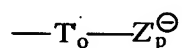
is not CH<sub>2</sub>CH(OSO<sub>3</sub><sup>-</sup>)R<sup>41</sup> wherein R<sup>41</sup> is selected from the group consisting of geminal dimethyl substituted alkyl, unsubstituted alkyl and phenyl.

Preferred aryliminium zwitterions having a net charge of from about +3 to about -3, as represented by the formula [XIV], include those of formula [XIV] where R<sup>25'</sup> is H or methyl, and  
15 for the radical, preferably non-linear radical, represented by the formula:



Z<sub>p</sub><sup>-</sup> is -CO<sub>2</sub><sup>-</sup>, -SO<sub>3</sub><sup>-</sup> or -OSO<sub>3</sub><sup>-</sup>, and p is 1, 2 or 3. Even more preferably, Z<sub>p</sub><sup>-</sup> is -SO<sub>3</sub><sup>-</sup> or -OSO<sub>3</sub><sup>-</sup>,  
20 and p is 1.

Also preferably,



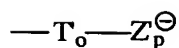
25 and/or the ring carbon(s) containing the groups R<sup>27'</sup> - R<sup>28'</sup>, when present, include branching at one or more of the following positions, when present, alpha, beta, gamma, delta and epsilon positions, although branching may or may not also be present at other positions.

More preferably,



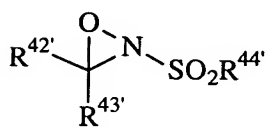
and/or the ring carbon(s) containing the groups R<sup>27'</sup> - R<sup>28'</sup>, when present, include branching at one or more of the following positions, when present, beta, gamma, delta and epsilon positions, although branching may or may not also be present at the alpha position, as well as at other  
35 positions.

Even more preferably,

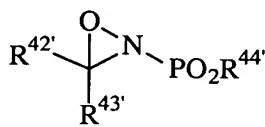


- 5 and/or the ring carbon(s) containing the groups  $R^{27'}$  -  $R^{28'}$ , when present, includes branching, when present, at the beta position, although branching may or may not also be present at the alpha, gamma, delta and epsilon positions, as well as at other positions.

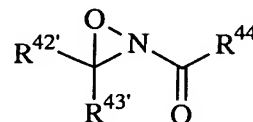
- c) Oxaziridine Sulfonimines, Phosphonimines, N-Acylimines, Thiodiazole Dioxides - The oxaziridine sulfonimines [XXIVa], phosphonimines [XXIVb], N-acylimines [XXV] and thiodiazole dioxides [XXVI] and [XXVII] are represented as follows:



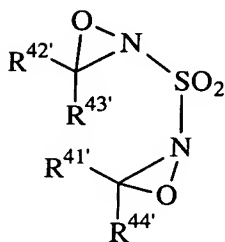
[XXIVa]



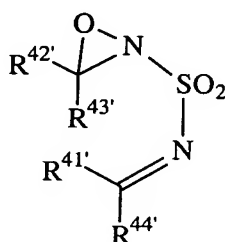
[XXIVb]



[XXV]



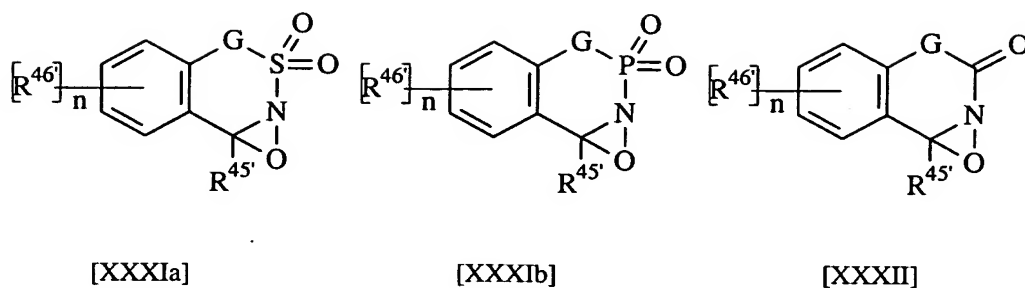
[XXVI]



[XXVII]

- 15 where  $R^{41'}$  -  $R^{44'}$ , when present, are independently selected from substituted or unsubstituted radicals selected from the group consisting of H, alkyl, cycloalkyl, aryl, alkaryl, aralkyl, heterocyclic ring, silyl, nitro, halo, cyano, sulfonato, alkoxy, keto, carboxylic, carboalkoxy radicals, provided that any of  $R^{41'}$  -  $R^{44'}$  may be joined together with any other  $R^{41'}$  -  $R^{44'}$  to form part of a common ring, including a fused aryl, fused carbocyclic or fused heterocyclic ring.

- 20 Preferably, the oxaziridine sulfonimines [XXXIa], phosphonimines [XXXIb], N-acylimines [XXXII] are represented as follows:



- 5 wherein n is an integer from 0 to 4; each R<sup>46'</sup> is independently selected from a substituted or unsubstituted radical selected from the group consisting of H, alkyl, cycloalkyl, aryl, fused aryl, heterocyclic ring, fused heterocyclic ring, nitro, halo, cyano, sulfonato, alkoxy, keto, carboxylic, and carboalkoxy radicals, and any two vicinal R<sup>46'</sup> substituents may combine to form a fused aryl, fused carbocyclic or fused heterocyclic ring; R<sup>45'</sup> may be a substituted or unsubstituted radical selected from the group consisting of H, alkyl, cycloalkyl, alkaryl, aryl, aralkyl, heterocyclic ring, silyl, nitro, halo, cyano, sulfonato, alkoxy, keto, carboxylic, and carboalkoxy radicals; G, when present, is selected from the group consisting of: (1) -O-; (2) -N(R<sup>47'</sup>)-; and (3) -N(R<sup>47'</sup>R<sup>48'</sup>)-; R<sup>47'</sup>-R<sup>48'</sup> are substituted or unsubstituted radicals independently selected from the group consisting of H, oxygen, linear or branched C<sub>1</sub>-C<sub>12</sub> alkyls, alkylenes, alkoxy, aryls, alkaryls, aralkyls, cycloalkyls, and heterocyclic rings; and

Suitable examples of X<sup>-</sup>, an anionic counterion, include, but are not limited to: BF<sub>4</sub><sup>-</sup>, OTS<sup>-</sup>, and other anionic counterions disclosed in WO 97/06147, WO 95/13352, WO 95/13353, WO 95/13351, WO 98/23717, U.S. Patent Nos. 5,360,568, 5,360,569, 5,482,515, 5,550,256, 5,478,357, 5,370,826, 5,442,066, EP 728 182 B1 and UK 1 215 656. Preferably, the anionic counterions are bleach-compatible.

For any structures that carry no net charge, no counterions are associated with the compound.

For any structures that carry a net negative charge, suitable examples of X<sup>+</sup>, a cationic counterion include, but are not limited to Na<sup>+</sup>, K<sup>+</sup>, H<sup>+</sup>.

- 25 For any structures that carry a net multiple charge, suitable examples of anionic and cationic counterions include, but are not limited to those described above.

Other Organic Catalyst Compounds - In addition to the bleach boosting compounds, bleaching species and modified amines and amine oxides disclosed above, organic catalyst compounds can be any compound known in the art that is capable of reacting with a peracid to form an oxygen transfer agent (a bleach).

Concentration of Organic Catalyst Compounds - The organic catalyst compounds of the present invention may be added to a wash solution in levels of from about 0.00001% (0.0001 ppm) to



about 10% (100 ppm) by weight of the composition, and preferably from about 0.0001% (0.001 ppm) to about 2% (20 ppm) by weight of the composition, more preferably from about 0.005% (0.05 ppm) to about 0.5% (5 ppm), even more preferably from about 0.01% (0.1 ppm) to about 0.2% (2 ppm). Most preferably from about 0.02% (0.2 ppm) to about 0.1% (1 ppm).

5 Preferably, the bleaching compositions of the present invention bleach composition comprise an amount of organic catalyst compound such that the resulting concentration of the bleach boosting compound in a wash solution is from about 0.001 ppm to about 5 ppm.

10 Further, preferably the bleach compositions of the present invention comprise an amount of peroxygen compound, when present, and an amount of organic catalyst compound, such that the resulting molar ratio of said peroxygen compound to organic catalyst compound in a wash solution is preferably greater than 1:1, more preferably greater than 10:1, even more preferably greater than 50:1. The preferred molar ratio ranges of peroxygen compound to cationic organic catalyst compound range from about 30,000:1 to about 10:1, even more preferably from about 15 10,000:1 to about 50:1, yet even more preferably from about 5,000:1 to about 100:1, still even more preferably from about 3,500:1 to about 150:1.

20 The conversion values (in ppm) are provided for exemplary purposes, based on an in-use product concentration of 1000 ppm. A 1000 ppm wash solution of a product containing 0.2% organic catalyst compound by weight results in a organic catalyst compound concentration of 2 ppm. Similarly, a 3500 ppm wash solution of a product containing 0.2% organic catalyst compound by weight results in a organic catalyst compound concentration of 6.5 ppm.

25 The method for delivering organic catalyst compounds of the present invention and the method for delivering bleaching compositions (products) containing such organic catalyst compounds that are particularly useful in the methods of the present invention are the organic catalyst compounds and compositions containing same that satisfy the preferred method for bleaching a stained substrate in an aqueous medium with a peroxygen source and with an organic catalyst compound whose structures is defined herein and wherein said medium contains active oxygen from the peroxygen compound from about 0.05 to about 250 ppm per liter of medium, and said organic catalyst compound from 0.001 ppm to about 5 ppm, preferably from about 0.01 ppm 30 to about 3 ppm, more preferably from about 0.1 ppm to about 2 ppm, and most preferably from about 0.2 ppm to about 1 ppm.

35 Such a preferred method for bleaching a stained substrate in an aqueous medium with a peroxygen source and with an organic catalyst compound is of particular value for those applications in which the color safety of the stained substrate in need of cleaning is a concern. In such applications the preferred embodiment (e.g., 0.01 ppm to about 3 ppm) is of particular

importance in terms of achieving acceptable fabric color safety. For other applications in which color safety of the stained substrate in need of cleaning is of less concern, a higher in-use concentration may be preferred.

#### ANIONIC SURFACTANTS

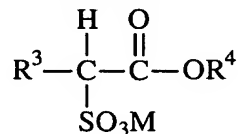
5 In addition to the organic catalyst compounds, the bleaching compositions of the present invention include one or more anionic surfactants. Preferably, the anionic surfactants are selected from the group consisting of linear alkylbenzene sulfonates, alpha olefin sulfonates, paraffin sulfonates, alkyl ester sulfonates, alkyl sulfates, alkyl alkoxy sulfates, alkyl sulfonates, alkyl alkoxy carboxylates, alkyl alkoxyated sulfates, sarcosinates, taurinates, and mixtures thereof. An  
10 effective amount, typically from about 0.5% to about 90%, preferably about 5% to about 60%, more preferably from about 10 to about 30%, by weight of anionic detergent surfactant is used in the bleaching compositions of the present invention.

Alkyl sulfate surfactants, especially when used in combination with polyhydroxy fatty acid amides (see below), provide excellent overall cleaning including good grease/oil cleaning  
15 over a wide range of temperatures, wash concentrations, and wash times. Suitable examples of alkyl sulfates useful in the bleaching compositions of the present invention include water soluble salts or acids of the formula  $\text{ROSO}_3\text{M}$  wherein R preferably is a  $\text{C}_{10}\text{-C}_{24}$  hydrocarbyl, more preferably an alkyl or hydroxyalkyl having a  $\text{C}_{10}\text{-C}_{20}$  alkyl component, most preferably a  $\text{C}_{12}\text{-C}_{18}$  alkyl or hydroxyalkyl, and M is H or a cation, e.g., an alkali (Group IA) metal cation (e.g.,  
20 sodium, potassium, lithium), substituted or unsubstituted ammonium cations such as methyl-, dimethyl-, and trimethyl ammonium and quaternary ammonium cations, e.g., tetramethyl-ammonium and dimethyl piperdinium, and cations derived from alkanolamines such as ethanolamine, diethanolamine, triethanolamine, and mixtures thereof, and the like. Typically, alkyl chains of  $\text{C}_{12}\text{-C}_{16}$  are preferred for lower wash temperatures (e.g., below about  $50^\circ\text{C}$ ) and  
25  $\text{C}_{16}\text{-C}_{18}$  alkyl chains are preferred for higher wash temperatures (e.g., above about  $50^\circ\text{C}$ ).

Alkyl alkoxyated sulfate surfactants are another category of useful anionic surfactants. These surfactants are water soluble salts or acids typically of the formula  $\text{RO(A)}_m\text{SO}_3\text{M}$  wherein R is preferably an unsubstituted  $\text{C}_{10}\text{-C}_{24}$  alkyl or hydroxyalkyl group having a  $\text{C}_{10}\text{-C}_{24}$  alkyl component, more preferably a  $\text{C}_{12}\text{-C}_{20}$  alkyl or hydroxyalkyl, most preferably a  $\text{C}_{12}\text{-C}_{18}$  alkyl  
30 or hydroxyalkyl, A is an ethoxy or propoxy unit, m is greater than zero, typically between about 0.5 and about 6, preferably between about 0.5 and about 3, and M is H or a cation which can be, for example, a metal cation (e.g., sodium, potassium, lithium, etc.), ammonium or substituted-ammonium cation. Alkyl ethoxylated sulfates as well as alkyl propoxylated sulfates are contemplated herein. Specific examples of substituted ammonium cations include methyl-,  
35 dimethyl-, trimethyl-ammonium and quaternary ammonium cations, such as tetramethyl-

ammonium, dimethyl piperidinium and cations derived from alkanolamines, e.g. monoethanolamine, diethanolamine, and triethanolamine, and mixtures thereof. Exemplary surfactants are C<sub>12</sub>-C<sub>18</sub> alkyl polyethoxylate (1.0) sulfate, C<sub>12</sub>-C<sub>18</sub> alkyl polyethoxylate (2.25) sulfate, C<sub>12</sub>-C<sub>18</sub> alkyl polyethoxylate (3.0) sulfate, and C<sub>12</sub>-C<sub>18</sub> alkyl polyethoxylate (4.0) sulfate wherein M is conveniently selected from sodium and potassium. Surfactants for use herein can be made from natural or synthetic alcohol feedstocks. Chain lengths represent average hydrocarbon distributions, including branching.

Alkyl ester sulfonate surfactants for use in the bleaching compositions of the present invention comprise alkyl ester sulfonate surfactants of the structural formula:



wherein R<sup>3</sup> is a C<sub>8</sub>-C<sub>20</sub> hydrocarbyl, preferably an alkyl, or combination thereof, R<sup>4</sup> is a C<sub>1</sub>-C<sub>6</sub> hydrocarbyl, preferably an alkyl, or combination thereof, and M is a cation which forms a water soluble salt with the alkyl ester sulfonate. Suitable salt-forming cations include metals such as sodium, potassium, and lithium, and substituted or unsubstituted ammonium cations, such as monoethanolamine, diethanolamine, and triethanolamine. Preferably, R<sup>3</sup> is C<sub>10</sub>-C<sub>16</sub> alkyl, and R<sup>4</sup> is methyl, ethyl or isopropyl. Especially preferred are the methyl ester sulfonates wherein R<sup>3</sup> is C<sub>10</sub>-C<sub>16</sub> alkyl. These alkyl ester sulfonate surfactants include linear esters of C<sub>8</sub>-C<sub>20</sub> carboxylic acids (i.e., fatty acids) which are sulfonated with gaseous SO<sub>3</sub> according to "The Journal of the American Oil Chemists Society", 52 (1975), pp. 323-329. Suitable starting materials for such alkyl ester sulfonated surfactants would include natural fatty substances derived from tallow, palm oil, etc.

The anionic surfactant for use in the present invention may include a mid-chain branched alkyl sulfate surfactant, a mid-chain branched alkyl alkoxylate surfactant, and/or a mid-chain branched alkyl alkoxylate sulfate surfactant. These surfactants are further described in No. 60/061,971, Attorney docket No 6881P October 14, 1997, No. 60/061,975, Attorney docket No 6882P October 14, 1997, No. 60/062,086, Attorney docket No 6883P October 14, 1997, No. 60/061,916, Attorney docket No 6884P October 14, 1997, No. 60/061,970, Attorney docket No 6885P October 14, 1997, No. 60/062,407, Attorney docket No 6886P October 14, 1997,. Other suitable mid-chain branched surfactants can be found in U.S. Patent applications Serial Nos. 60/032,035 (Docket No. 6401P), 60/031,845 (Docket No. 6402P), 60/031,916 (Docket No. 6403P), 60/031,917 (Docket No. 6404P), 60/031,761 (Docket No. 6405P), 60/031,762 (Docket No. 6406P) and 60/031,844 (Docket No. 6409P). Mixtures of these branched surfactants with conventional linear surfactants are also suitable for use in the present compositions.

Modified alkyl benzene sulfonate surfactants ("MLAS") are also useful anionic surfactants for incorporation into the bleaching compositions of the present invention. Some suitable MLAS surfactants, methods of making them and exemplary compositions are further described in copending U.S. Patent application Serial Nos. 60/053,319 (Docket No. 6766P), 60/053,318 (Docket No. 6767P), 60/053,321 (Docket No. 6768P), 60/053,209 (Docket No. 6769P), 60/053,328 (Docket No. 6770P), 60/053,186 (Docket No. 6771P), 60/055,437 (Docket No. 6796P), 60/105,017 (Docket No. 7303P), and 60/104,962 (Docket No. 7304P).

Additional examples of suitable anionic surfactants are given in "Surface Active Agents and Detergents" (Vol. I and II by Schwartz, Perry and Berch). A variety of anionic surfactants are also generally disclosed in U.S. Patent 3,929,678, issued December 30, 1975 to Laughlin, et al. at Column 23, line 58 through Column 29, line 23.

The bleaching compositions of the present invention typically comprise from about 1%, preferably from about 3% to about 40%, preferably about 20% by weight of one or more anionic surfactants.

#### 15 DECOMPOSITION OF ORGANIC CATALYSTS

The organic catalysts, specifically the bleach boosting compounds of the present invention are susceptible to decomposition by various decomposition pathways including, but not limited to, the aromatization pathway. The aromatization (decomposition) reaction of 6-membered ring boosters is well known in the art, as exemplified, without being limited by theory, in Hanquet et al., *Tetrahedron* **1993**, 49, pp. 423-438. Other means of decomposition include, but are not limited to, attack on the bleach boosting compound and/or on the bleaching species by nucleophiles, including but not limited to attack by hydroxide anion, perhydroxide anion, carboxylate anion, percarboxylate anion and other nucleophiles present under in-wash conditions. For example, and without intending to be bound by theory, the decomposition reaction of a 6-membered ring oxaziridinium, the overall process of which can lead to reduced bleaching efficiency, is exemplified as set forth below:



#### 30 METHODS FOR DELAYED (CONTROLLED) ADDITION OF ORGANIC CATALYST COMPOUNDS

It has surprisingly been found with organic catalyst compounds of limited lifetime, that the addition of organic catalyst compounds by a delivery means to a wash solution after a fabric

has been added to a wash solution provides enhanced bleaching compared to the addition of such organic catalyst compounds to the wash solution before a fabric has been added to the wash solution. It is believed, without being limited by theory, that the organic catalyst compound undergoes decomposition in the wash solution prior to the introduction of the fabric load. One method for improving the performance of organic catalyst compounds is to delay (control) the addition of the organic catalyst compound of the present invention to the wash solution. Methods for delayed (controlled) addition of organic catalyst compounds are more fully described in copending and co-owned U.S. Provisional Patent Application entitled "Controlled Availability of Formulation Components, Compositions and Laundry Methods Employing Same" filed August 27, 1999 (P&G Attorney Docket Number 7749P).

Another method of improving the performance of organic catalyst compounds is to use an organic catalyst compound with increased stability to the wash conditions. This application describes a method of improving the performance of organic catalyst compounds by bleaching compositions comprising organic catalyst compounds, specifically bleach boosting compounds, more specifically bleach boosters and/or bleaching species, in combination with an anionic surfactant that perform effective bleaching at lower water temperatures.

This application describes organic catalyst compounds which may fall in either category, having a short or long lifetime, and as such can be added prior to or after the introduction of the fabric, depending on the desired application and desired bleaching result in terms of overall performance and color safety.

#### BLEACHING COMPOSITIONS COMPRISING ORGANIC CATALYST COMPOUNDS

In addition to the use of organic catalyst compounds discussed above, the organic catalyst compounds of the present invention may be employed in conjunction with a peroxygen source in other bleaching compositions, regardless of their form. For example, the organic catalyst compounds may be employed in a laundry additive product. In the bleaching compositions of the present invention, the peroxygen source may be present in levels of from about 0.1% to about 60% by weight of the composition, and preferably from about 1% to about 40% by weight of the composition. In a composition, the organic catalyst may be present from about 0.001% to about 10% by weight of the composition, and more preferably from about 0.005% to about 5% by weight of the composition.

The bleaching compositions of the present invention may be advantageously employed in laundry applications, hard surface cleaning, automatic dishwashing applications, as well as cosmetic applications such as dentures, teeth, hair and skin. However, due to the unique advantages of increased effectiveness in cold and possibly warm water solutions due to possible increased stability, the organic catalyst compounds of the present invention are ideally suited for

laundry applications such as the bleaching of fabrics through the use of bleach-containing detergents or laundry bleach additives. Furthermore, the organic catalyst compounds of the present invention may be employed in both granular and liquid compositions.

Accordingly, the bleaching compositions of the present invention may include various additional ingredients which are desirable in laundry applications. Such ingredients include  
5     detergent surfactants, bleach catalysts, builders, chelating agents, enzymes, polymeric soil release agents, brighteners and various other ingredients. Compositions including any of these various additional ingredients preferably have a pH of from about 6 to about 12, preferably from about 8 to about 10.5 in a 1% solution of the bleaching composition.

10     The bleaching compositions preferably include at least one detergent surfactant, at least one chelating agent, at least one detergent enzyme and preferably has a pH of about 6 to about 12, preferably from about 8 to about 10.5 in a 1% solution of the bleaching composition.

In another embodiment of the present invention, a method for laundering a fabric in need of laundering is provided. The preferred method comprises contacting the fabric with a laundry  
15     solution. The fabric may comprise most any fabric capable of being laundered in normal consumer use conditions. The laundry solution comprises a bleaching composition, as fully described herein. The water temperatures preferably range from about 0 °C to about 50 °C or higher. The water to fabric ratio is preferably from about 1:1 to about 15:1.

20     The laundry solution may further include at least one additional ingredient selected from the group consisting of detergent surfactants, chelating agents, detergent enzymes and mixtures thereof. Preferably, the laundry solution has a pH of about 6 to about 12, preferably from about 8 to about 10.5 in a 1% solution of the bleaching composition.

In accordance with another aspect of the present invention, a laundry additive product is provided. The laundry additive product comprises an organic catalyst compound, as fully  
25     described above. Such a laundry additive product would be ideally suited for inclusion in a wash process when additional bleaching effectiveness is desired. Such instances may include, but are not limited to, low-temperature and medium temperature solution laundry application.

It is desirable that the laundry additive product further includes a peroxygen source, as fully described above. The laundry additive product can also include powdered or liquid  
30     compositions containing a hydrogen peroxide source or a peroxygen source as fully defined above.

Furthermore, if the laundry additive product includes a hydrogen peroxide source, it is desirable that the laundry additive product further includes a bleach activator, as fully described above.

Preferably, the laundry additive product is packaged in dosage form for addition to a  
35     laundry process where a source of peroxygen is employed and increased bleaching effectiveness is

desired. Such single dosage form may comprise a pill, tablet, gelcap or other single dosage unit such as pre-measured powders or liquids. A filler or carrier material may be included to increase the volume of composition if desired. Suitable filler or carrier materials may be selected from but not limited to various salts of sulfate, carbonate and silicate as well as talc, clay and the like.

- 5 Filler or carrier materials for liquid compositions may be water or low molecular weight primary and secondary alcohols including polyols and diols. Examples include methanol, ethanol, propanol and isopropanol. Monohydric alcohols may also be employed. The compositions may contain from about 5% to about 90% of such materials. Acidic fillers can be used to reduce pH.

A preferred bleaching composition is a bleaching composition comprising:

10

- (a) a peroxygen source;
- (b) one or more organic catalyst compounds; and
- (c) one or more anionic surfactants.

- 15 The peroxygen source, like discussed above, is preferably selected from the group consisting of:

(i) preformed peracid compounds selected from the group consisting of percarboxylic acids and salts, percarbonic acids and salts, perimidic acids and salts, peroxymonosulfuric acids and salts, and mixtures thereof, and

- 20 (ii) hydrogen peroxide sources selected from the group consisting of perborate compounds, percarbonate compounds, perphosphate compounds and mixtures thereof, and a bleach activator.

Preferably, the peroxygen source is selected from hydrogen peroxide sources selected from the group consisting of perborate compounds, percarbonate compounds, perphosphate compounds and mixtures thereof, and a bleach activator.

25

More preferably, the bleach activator is selected from the group consisting of hydrophobic bleach activators as disclosed herein.

The period of time between the peracid becoming active in a wash solution and the organic catalyst compounds becoming active can be in the range of from about 1 second to about 24 hours.

30

The purpose of a delayed addition bleaching composition (which may or may not be used in conjunction with this invention) is to allow the peracid to achieve maximum bleaching performance on a fabric in need of cleaning, such as a stained fabric, in a wash solution prior to the introduction of the organic catalyst compound. In other words, a bleaching composition comprising a organic catalyst compound which becomes active in a wash solution after a fabric in

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need of cleaning has been added to the wash solution. Alternatively, since the organic catalyst compounds can have increased stability, a bleaching composition comprising an organic catalyst compound which becomes active in a wash solution prior to a fabric in need of cleaning has been added to the wash solution may be used.

5       The bleaching compositions of the present invention also comprise, in addition to one or more organic catalysts, described hereinbefore, one or more cleaning adjunct materials, preferably compatible with the organic catalyst(s) and/or any enzymes present in the bleaching composition. The term "compatible", as used herein, means the bleaching composition materials do not reduce the bleaching activity of the organic catalyst and/or any enzymatic activity of any enzyme present  
10       in the bleaching composition to such an extent that the organic catalyst and/or enzyme is not effective as desired during normal use situations. The term "cleaning adjunct materials", as used herein, means any liquid, solid or gaseous material selected for the particular type of bleaching composition desired and the form of the product (e.g., liquid; granule; powder; bar; paste; spray; tablet; gel; foam composition), which materials are also preferably compatible with the protease  
15       enzyme(s) and bleaching agent(s) used in the composition. Granular compositions can also be in "compact" form and the liquid compositions can also be in a "concentrated" form.

      The specific selection of cleaning adjunct materials are readily made by considering the surface, item or fabric to be cleaned, and the desired form of the composition for the cleaning conditions during use (e.g., through the wash detergent use). Examples of suitable cleaning  
20       adjunct materials include, but are not limited to, surfactants, builders, bleaches, bleach activators, bleach catalysts, other enzymes, enzyme stabilizing systems, chelants, optical brighteners, soil release polymers, dye transfer agents, dispersants, suds suppressors, dyes, perfumes, colorants, filler salts, hydrotropes, photoactivators, fluorescers, fabric conditioners, hydrolyzable surfactants, perservatives, anti-oxidants, anti-shrinkage agents, anti-wrinkle agents, germicides, fungicides,  
25       color speckles, silvercare, anti-tarnish and/or anti-corrosion agents, alkalinity sources, solubilizing agents, carriers, processing aids, pigments and pH control agents as described in U.S. Patent Nos. 5,705,464, 5,710,115, 5,698,504, 5,695,679, 5,686,014 and 5,646,101. Specific bleaching composition materials are exemplified in detail hereinafter.

      If the cleaning adjunct materials are not compatible with the protease variant(s) in the  
30       bleaching compositions, then suitable methods of keeping the cleaning adjunct materials and the protease variant(s) separate (not in contact with each other) until combination of the two components is appropriate can be used. Suitable methods can be any method known in the art, such as gelpcaps, encapsulation, tablets, physical separation, etc.

      Such bleaching compositions include detergent compositions for cleaning hard surfaces,  
35       unlimited in form (e.g., liquid, granular, paste, foam, spray, etc.); detergent compositions for



cleaning fabrics, unlimited in form (e.g., granular, liquid, bar formulations, etc.); dishwashing compositions (unlimited in form and including both granular and liquid automatic dishwashing); oral bleaching compositions, unlimited in form (e.g., dentifrice, toothpaste and mouthwash formulations); and denture bleaching compositions, unlimited in form (e.g., liquid, tablet).

5       The fabric bleaching compositions of the present invention are mainly intended to be used in the wash cycle of a washing machine; however, other uses can be contemplated, such as pretreatment product for heavily-soiled fabrics, or soaking product; the use is not necessarily limited to the washing-machine context, and the compositions of the present invention can be used alone or in combination with compatible handwash compositions.

10       The bleaching compositions may include from about 1% to about 99.9% by weight of the composition of the cleaning adjunct materials.

As used herein, "non-fabric bleaching compositions" include hard surface bleaching compositions, dishwashing compositions, oral bleaching compositions, denture bleaching compositions and personal cleansing compositions.

15       When the bleaching compositions of the present invention are formulated as compositions suitable for use in a laundry machine washing method, the compositions of the present invention preferably contain both a surfactant and a builder compound and additionally one or more cleaning adjunct materials preferably selected from organic polymeric compounds, bleaching agents, additional enzymes, suds suppressors, dispersants, lime-soap dispersants, soil suspension and anti-redeposition agents and corrosion inhibitors. Laundry compositions can also contain softening agents, as additional cleaning adjunct materials.

20       The compositions of the present invention can also be used as detergent additive products in solid or liquid form. Such additive products are intended to supplement or boost the performance of conventional detergent compositions and can be added at any stage of the cleaning process.

25       When formulated as compositions for use in manual dishwashing methods the compositions of the invention preferably contain a surfactant and preferably other cleaning adjunct materials selected from organic polymeric compounds, suds enhancing agents, group II metal ions, solvents, hydrotropes and additional enzymes.

30       If needed the density of the laundry detergent compositions herein ranges from 400 to 1200 g/litre, preferably 500 to 950 g/litre of composition measured at 20 °C.

35       The "compact" form of the bleaching compositions herein is best reflected by density and, in terms of composition, by the amount of inorganic filler salt; inorganic filler salts are conventional ingredients of detergent compositions in powder form; in conventional detergent compositions, the filler salts are present in substantial amounts, typically 17-35% by weight of the

total composition. In the compact compositions, the filler salt is present in amounts not exceeding 15% of the total composition, preferably not exceeding 10%, most preferably not exceeding 5% by weight of the composition. The inorganic filler salts, such as meant in the present compositions are selected from the alkali and alkaline-earth-metal salts of sulfates and chlorides.

5 A preferred filler salt is sodium sulfate.

Liquid bleaching compositions according to the present invention can also be in a "concentrated form", in such case, the liquid bleaching compositions according the present invention will contain a lower amount of water, compared to conventional liquid detergents. Typically the water content of the concentrated liquid bleaching composition is preferably less than 40%, more preferably less than 30%, most preferably less than 20% by weight of the bleaching composition.

#### Cleaning Adjunct Materials

While not essential for the purposes of the present invention, several conventional cleaning adjunct materials illustrated hereinafter are suitable for use in the instant bleaching compositions and may be desirably incorporated in preferred embodiments of the invention, for example to assist or enhance cleaning performance, for treatment of the substrate to be cleaned, or to modify the aesthetics of the bleaching composition as is the case with perfumes, colorants, dyes or the like. The precise nature of these additional components, and levels of incorporation thereof, will depend on the physical form of the composition and the nature of the cleaning operation for which it is to be used. Unless otherwise indicated, the bleaching compositions of the invention may for example, be formulated as granular or powder-form all-purpose or "heavy-duty" washing agents, especially laundry detergents; liquid, gel or paste-form all-purpose washing agents, especially the so-called heavy-duty liquid types; liquid fine-fabric detergents; hand dishwashing agents or light duty dishwashing agents, especially those of the high-foaming type; machine dishwashing agents, including the various tablet, granular, liquid and rinse-aid types for household and institutional use; liquid cleaning and disinfecting agents, including antibacterial hand-wash types, laundry bars, mouthwashes, denture cleaners, car or carpet shampoos, bathroom cleaners; hair shampoos and hair-rinses; shower gels and foam baths and metal cleaners; as well as cleaning auxiliaries such as bleach additives and "stain-stick" or pre-treat types.

30 Surfactant System - Other deterative surfactants, in addition to the anionic surfactants discussed above, can be included in the fully-formulated bleaching compositions afforded by the present invention such that the surfactant system comprises at least 0.01%, preferably at least about 0.1%, more preferably at least about 0.5%, most preferably at least about 1% to about 60%, more preferably to about 35%, most preferably to about 30% by weight of the bleaching composition depending upon the particular surfactants used and the desired effects.

The deterative surfactant can be nonionic, anionic, ampholytic, zwitterionic, cationic, semi-polar nonionic, and mixtures thereof, nonlimiting examples of which are disclosed in U.S. Patent Nos. 5,707,950 and 5,576,282. Preferred detergent and bleaching compositions comprise anionic deterative surfactants or mixtures of anionic surfactants with other surfactants, especially nonionic surfactants.

Anionic surfactants are highly preferred for use with the organic catalysts and bleaching compositions of the present invention.

Nonlimiting examples of surfactants useful herein include the conventional C<sub>11</sub>-C<sub>18</sub> alkyl benzene sulfonates and primary, secondary and random alkyl sulfates, the C<sub>10</sub>-C<sub>18</sub> alkyl alkoxy sulfates, the C<sub>10</sub>-C<sub>18</sub> alkyl polyglycosides and their corresponding sulfated polyglycosides, C<sub>12</sub>-C<sub>18</sub> alpha-sulfonated fatty acid esters, C<sub>12</sub>-C<sub>18</sub> alkyl and alkyl phenol alkoxyates (especially ethoxyates and mixed ethoxy/propoxy), C<sub>12</sub>-C<sub>18</sub> betaines and sulfobetaines ("sultaines"), C<sub>10</sub>-C<sub>18</sub> amine oxides, and the like. Other conventional useful surfactants are listed in standard texts.

The surfactant system is preferably formulated to be compatible with enzyme components present in the composition. In liquid or gel compositions the surfactant is most preferably formulated such that it promotes, or at least does not degrade, the stability of any enzyme in these compositions.

Nonionic Surfactants - Polyethylene, polypropylene, and polybutylene oxide condensates of alkyl phenols are suitable for use as the nonionic surfactant of the surfactant systems of the present invention, with the polyethylene oxide condensates being preferred. Commercially available nonionic surfactants of this type include Igepal<sup>TM</sup> CO-630, marketed by the GAF Corporation; and Triton<sup>TM</sup> X-45, X-114, X-100 and X-102, all marketed by the Rohm & Haas Company. These surfactants are commonly referred to as alkylphenol alkoxyates (e.g., alkyl phenol ethoxyates).

The condensation products of primary and secondary aliphatic alcohols with from about 1 to about 25 moles of ethylene oxide are suitable for use as the nonionic surfactant of the nonionic surfactant systems of the present invention. Examples of commercially available nonionic surfactants of this type include Tergitol<sup>TM</sup> 15-S-9 (the condensation product of C<sub>11</sub>-C<sub>15</sub> linear alcohol with 9 moles ethylene oxide), Tergitol<sup>TM</sup> 24-L-6 NMW (the condensation product of C<sub>12</sub>-C<sub>14</sub> primary alcohol with 6 moles ethylene oxide with a narrow molecular weight distribution), both marketed by Union Carbide Corporation; Neodol<sup>TM</sup> 45-9 (the condensation product of C<sub>14</sub>-C<sub>15</sub> linear alcohol with 9 moles of ethylene oxide), Neodol<sup>TM</sup> 23-3 (the condensation product of C<sub>12</sub>-C<sub>13</sub> linear alcohol with 3.0 moles of ethylene oxide), Neodol<sup>TM</sup> 45-7 (the condensation product of C<sub>14</sub>-C<sub>15</sub> linear alcohol with 7 moles of ethylene oxide), Neodol<sup>TM</sup> 45-5 (the condensation product of C<sub>14</sub>-C<sub>15</sub> linear alcohol with 5 moles of ethylene

oxide) marketed by Shell Chemical Company, Kyro<sup>TM</sup> EOB (the condensation product of C<sub>13</sub>-C<sub>15</sub> alcohol with 9 moles ethylene oxide), marketed by The Procter & Gamble Company, and Genapol LA O3O or O5O (the condensation product of C<sub>12</sub>-C<sub>14</sub> alcohol with 3 or 5 moles of ethylene oxide) marketed by Hoechst. Preferred range of HLB in these products is from 8-11 and most preferred from 8-10.

Also useful as the nonionic surfactant of the surfactant systems of the present invention are the alkylpolysaccharides disclosed in U.S. Patent No. 4,565,647.

Preferred alkylpolyglycosides have the formula:  $R^2O(C_nH_{2n}O)_t(\text{glycosyl})_x$

wherein R<sup>2</sup> is selected from the group consisting of alkyl, alkylphenyl, hydroxyalkyl, hydroxyalkylphenyl, and mixtures thereof in which the alkyl groups contain from about 10 to about 18, preferably from about 12 to about 14, carbon atoms; n is 2 or 3, preferably 2; t is from 0 to about 10, preferably 0; and x is from about 1.3 to about 10, preferably from about 1.3 to about 3, most preferably from about 1.3 to about 2.7.

The condensation products of ethylene oxide with a hydrophobic base formed by the condensation of propylene oxide with propylene glycol are also suitable for use as the additional nonionic surfactant systems of the present invention. Examples of compounds of this type include certain of the commercially-available Plurafac<sup>TM</sup> LF404 and Pluronic<sup>TM</sup> surfactants, marketed by BASF.

Also suitable for use as the nonionic surfactant of the nonionic surfactant system of the present invention, are the condensation products of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylenediamine. Examples of this type of nonionic surfactant include certain of the commercially available Tetronic<sup>TM</sup> compounds, marketed by BASF.

Preferred for use as the nonionic surfactant of the surfactant systems of the present invention are polyethylene oxide condensates of alkyl phenols, condensation products of primary and secondary aliphatic alcohols with from about 1 to about 25 moles of ethylene oxide, alkylpolysaccharides, and mixtures thereof. Most preferred are C<sub>8</sub>-C<sub>14</sub> alkyl phenol ethoxylates having from 3 to 15 ethoxy groups and C<sub>8</sub>-C<sub>18</sub> alcohol ethoxylates (preferably C<sub>10</sub> avg.) having from 2 to 10 ethoxy groups, and mixtures thereof.

Highly preferred nonionic surfactants are polyhydroxy fatty acid amide surfactants of the formula: R<sup>2</sup> - C(O) - N(R<sup>1</sup>) - Z wherein R<sup>1</sup> is H, or R<sup>1</sup> is C<sub>1-4</sub> hydrocarbyl, 2-hydroxy ethyl, 2-hydroxy propyl or a mixture thereof, R<sup>2</sup> is C<sub>5-31</sub> hydrocarbyl, and Z is a polyhydroxyhydrocarbyl having a linear hydrocarbyl chain with at least 3 hydroxyls directly connected to the chain, or an alkoxyated derivative thereof. Preferably, R<sup>1</sup> is methyl, R<sup>2</sup> is a straight C<sub>11-15</sub> alkyl or C<sub>16-18</sub> alkyl or alkenyl chain such as coconut alkyl or mixtures thereof, and Z is derived from a reducing sugar such as glucose, fructose, maltose, lactose, in a reductive amination reaction.

Cationic Surfactants - Cationic deterative surfactants suitable for use in the bleaching compositions of the present invention are those having one long-chain hydrocarbonyl group. Examples of such cationic surfactants include the ammonium surfactants such as alkyltrimethylammonium halogenides, and those surfactants having the formula:

5  $[R^2(OR^3)_y][R^4(OR^3)_y]_2R^5N^+X^-$  wherein  $R^2$  is an alkyl or alkyl benzyl group having from about 8 to about 18 carbon atoms in the alkyl chain, each  $R^3$  is selected from the group consisting of  $-CH_2CH_2-$ ,  $-CH_2CH(CH_3)-$ ,  $-CH_2CH(CH_2OH)-$ ,  $-CH_2CH_2CH_2-$ , and mixtures thereof; each  $R^4$  is selected from the group consisting of  $C_1$ - $C_4$  alkyl,  $C_1$ - $C_4$  hydroxyalkyl, benzyl ring structures formed by joining the two  $R^4$  groups,  $-CH_2CHOH-CHOHCOR^6CHOHCH_2OH$

10 wherein  $R^6$  is any hexose or hexose polymer having a molecular weight less than about 1000, and hydrogen when  $y$  is not 0;  $R^5$  is the same as  $R^4$  or is an alkyl chain wherein the total number of carbon atoms of  $R^2$  plus  $R^5$  is not more than about 18; each  $y$  is from 0 to about 10 and the sum of the  $y$  values is from 0 to about 15; and  $X$  is any compatible anion.

Highly preferred cationic surfactants are the water-soluble quaternary ammonium compounds useful in the present composition having the formula (i):  $R_1R_2R_3R_4N^+X^-$

15 wherein  $R_1$  is  $C_8$ - $C_{16}$  alkyl, each of  $R_2$ ,  $R_3$  and  $R_4$  is independently  $C_1$ - $C_4$  alkyl,  $C_1$ - $C_4$  hydroxy alkyl, benzyl, and  $-(C_2H_4O)_xH$  where  $x$  has a value from 2 to 5, and  $X$  is an anion. Not more than one of  $R_2$ ,  $R_3$  or  $R_4$  should be benzyl. The preferred alkyl chain length for  $R_1$  is  $C_{12}$ - $C_{15}$  particularly where the alkyl group is a mixture of chain lengths derived from coconut or palm

20 kernel fat or is derived synthetically by olefin build up or OXO alcohols synthesis. Preferred groups for  $R_2$ ,  $R_3$  and  $R_4$  are methyl and hydroxyethyl groups and the anion  $X$  may be selected from halide, methosulfate, acetate and phosphate ions.

Examples of suitable quaternary ammonium compounds of formulae (i) for use herein are include, but are not limited to: coconut trimethyl ammonium chloride or bromide; coconut methyl

25 dihydroxyethyl ammonium chloride or bromide; decyl triethyl ammonium chloride; decyl dimethyl hydroxyethyl ammonium chloride or bromide;  $C_{12-15}$  dimethyl hydroxyethyl ammonium chloride or bromide; coconut dimethyl hydroxyethyl ammonium chloride or bromide; myristyl trimethyl ammonium methyl sulphate; lauryl dimethyl benzyl ammonium chloride or bromide; lauryl dimethyl (ethenoxy) $_4$  ammonium chloride or bromide; choline esters

30 (compounds of formula (i) wherein  $R_1$  is

$$CH_2-CH_2-O-\overset{\overset{O}{||}}{C}-C_{12-14} \text{ alkyl}$$

and  $R_2, R_3$  and  $R_4$  are methyl); and di-alkyl imidazolines [(i)].

Other cationic surfactants useful herein are also described in U.S. Patent 4,228,044, Cambre, issued October 14, 1980 and in European Patent Application EP 000,224.

When included therein, the bleaching compositions of the present invention typically comprise from about 0.2%, preferably from about 1% to about 25%, preferably to about 8% by weight of such cationic surfactants.

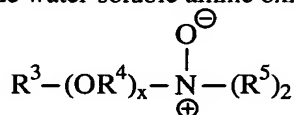
- 5     Ampholytic Surfactants - Ampholytic surfactants, examples of which are described in U.S. Patent No. 3,929,678, are also suitable for use in the bleaching compositions of the present invention.

When included therein, the bleaching compositions of the present invention typically comprise from about 0.2%, preferably from about 1% to about 15%, preferably to about 10% by weight of such ampholytic surfactants.

- 10     Zwitterionic Surfactants - Zwitterionic surfactants, examples of which are described in U.S. Patent No. 3,929,678, are also suitable for use in bleaching compositions.

When included therein, the bleaching compositions of the present invention typically comprise from about 0.2%, preferably from about 1% to about 15%, preferably to about 10% by weight of such zwitterionic surfactants.

- 15     Semi-polar Nonionic Surfactants - Semi-polar nonionic surfactants are a special category of nonionic surfactants which include water-soluble amine oxides having the formula:



- wherein R<sup>3</sup> is an alkyl, hydroxyalkyl, or alkyl phenyl group or mixtures thereof containing from about 8 to about 22 carbon atoms; R<sup>4</sup> is an alkylene or hydroxyalkylene group containing from about 2 to about 3 carbon atoms or mixtures thereof; x is from 0 to about 3; and each R<sup>5</sup> is an alkyl or hydroxyalkyl group containing from about 1 to about 3 carbon atoms or a polyethylene oxide group containing from about 1 to about 3 ethylene oxide groups (the R<sup>5</sup> groups can be attached to each other, e.g., through an oxygen or nitrogen atom, to form a ring structure); water-soluble phosphine oxides containing one alkyl moiety of from about 10 to about 18 carbon atoms and 2 moieties selected from the group consisting of alkyl groups and hydroxyalkyl groups containing from about 1 to about 3 carbon atoms; and water-soluble sulfoxides containing one alkyl moiety of from about 10 to about 18 carbon atoms and a moiety selected from the group consisting of alkyl and hydroxyalkyl moieties of from about 1 to about 3 carbon atoms.

- 25     The amine oxide surfactants in particular include C<sub>10</sub>-C<sub>18</sub> alkyl dimethyl amine oxides and C<sub>8</sub>-C<sub>12</sub> alkoxy ethyl dihydroxy ethyl amine oxides.

When included therein, the cleaning compositions of the present invention typically comprise from about 0.2%, preferably from about 1% to about 15%, preferably to about 10% by weight of such semi-polar nonionic surfactants.

Cosurfactants - The bleaching compositions of the present invention may further comprise a cosurfactant selected from the group of primary or tertiary amines. Suitable primary amines for use herein include amines according to the formula  $R_1NH_2$  wherein  $R_1$  is a  $C_6$ - $C_{12}$ , preferably  $C_6$ - $C_{10}$  alkyl chain or  $R_4X(CH_2)_n$ , X is -O-, -C(O)NH- or -NH-,  $R_4$  is a  $C_6$ - $C_{12}$  alkyl chain n is between 1 to 5, preferably 3.  $R_1$  alkyl chains may be straight or branched and may be interrupted with up to 12, preferably less than 5 ethylene oxide moieties.

Preferred amines according to the formula herein above are n-alkyl amines. Suitable amines for use herein may be selected from 1-hexylamine, 1-octylamine, 1-decylamine and laurylamine. Other preferred primary amines include  $C_8$ - $C_{10}$  oxypropylamine, octyloxypropylamine, 2-ethylhexyl-oxypropylamine, lauryl amido propylamine and amido propylamine. The most preferred amines for use in the compositions herein are 1-hexylamine, 1-octylamine, 1-decylamine, 1-dodecylamine. Especially desirable are n-dodecyldimethylamine and bishydroxyethylcoconutalkylamine and oleylamine 7 times ethoxylated, lauryl amido propylamine and cocoamido propylamine.

LFNIs - Particularly preferred surfactants in the automatic dishwashing compositions (ADD) of the present invention are low foaming nonionic surfactants (LFNI) which are described in U.S. Patent Nos. 5,705,464 and 5,710,115. LFNI may be present in amounts from 0.01% to about 10% by weight, preferably from about 0.1% to about 10%, and most preferably from about 0.25% to about 4%. LFNIs are most typically used in ADDs on account of the improved water-sheeting action (especially from glass) which they confer to the ADD product. They also encompass non-silicone, nonphosphate polymeric materials further illustrated hereinafter which are known to defoam food soils encountered in automatic dishwashing.

Preferred LFNIs include nonionic alkoxylated surfactants, especially ethoxylates derived from primary alcohols, and blends thereof with more sophisticated surfactants, such as the polyoxypropylene/polyoxyethylene/polyoxypropylene (PO/EO/PO) reverse block polymers as described in U.S. Patent Nos. 5,705,464 and 5,710,115.

LFNIs which may also be used include those POLY-TERGENT® SLF-18 nonionic surfactants from Olin Corp., and any biodegradable LFNI having the melting point properties discussed hereinabove.

These and other nonionic surfactants are well known in the art, being described in more detail in Kirk Othmer's Encyclopedia of Chemical Technology, 3rd Ed., Vol. 22, pp. 360-379, "Surfactants and Detergent Systems", incorporated by reference herein.

Bleaching System - In addition to the organic catalyst of the present invention, the bleaching compositions of the present invention preferably comprise a bleaching system. Bleaching systems typically comprise a peroxygen source. Peroxygen sources are well-known in

the art and the peroxygen source employed in the present invention may comprise any of these well known sources, including peroxygen compounds as well as compounds which under consumer use conditions provide an effective amount of peroxygen in situ. The peroxygen source may include a hydrogen peroxide source, the in situ formation of a peracid anion through the reaction of a hydrogen peroxide source and a bleach activator, preformed peracid compounds or mixtures of suitable peroxygen sources. Of course, one of ordinary skill in the art will recognize that other sources of peroxygen may be employed without departing from the scope of the invention. Preferably, the peroxygen source is selected from the group consisting of:

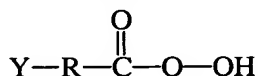
(i) preformed peracid compounds selected from the group consisting of percarboxylic acids and salts, percarbonic acids and salts, perimidic acids and salts, peroxymonosulfuric acids and salts, and mixtures thereof, and

(ii) hydrogen peroxide sources selected from the group consisting of perborate compounds, percarbonate compounds, perphosphate compounds and mixtures thereof, and a bleach activator.

When present, peroxygen sources (peracids and/or hydrogen peroxide sources) will typically be at levels of from about 1%, preferably from about 5% to about 30%, preferably to about 20% by weight of the composition. If present, the amount of bleach activator will typically be from about 0.1%, preferably from about 0.5% to about 60%, preferably to about 40% by weight, of the bleaching composition comprising the bleaching agent-plus-bleach activator.

a. Preformed Peracids - The preformed peracid compound as used herein is any convenient compound which is stable and which under consumer use conditions provides an effective amount of peracid anion. The organic catalyst compounds of the present invention may of course be used in conjunction with a preformed peracid compound selected from the group consisting of percarboxylic acids and salts, percarbonic acids and salts, perimidic acids and salts, peroxymonosulfuric acids and salts, and mixtures thereof, examples of which are described in U.S. Patent No. 5,576,282 to Miracle et al.

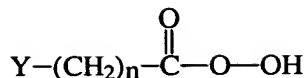
One class of suitable organic peroxydicarboxylic acids have the general formula:



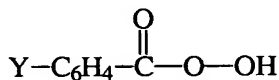
wherein R is an alkylene or substituted alkylene group containing from 1 to about 22 carbon atoms or a phenylene or substituted phenylene group, and Y is hydrogen, halogen, alkyl, aryl, -C(O)OH or -C(O)OOH.

Organic peroxyacids suitable for use in the present invention can contain either one or two peroxy groups and can be either aliphatic or aromatic. When the organic peroxydicarboxylic acid is aliphatic, the unsubstituted peracid has the general formula:





where Y can be, for example, H, CH<sub>3</sub>, CH<sub>2</sub>Cl, C(O)OH, or C(O)OOH; and n is an integer from 0 to 20. When the organic peroxydicarboxylic acid is aromatic, the unsubstituted peracid has the general formula:



wherein Y can be, for example, hydrogen, alkyl, alkylhalogen, halogen, C(O)OH or C(O)OOH.

Typical monoperoxy acids useful herein include alkyl and aryl peroxyacids such as:

(i) peroxybenzoic acid and ring-substituted peroxybenzoic acid, e.g. peroxy-*a*-naphthoic acid, monoperoxyphthalic acid (magnesium salt hexahydrate), and *o*-carboxybenzamidoperoxyhexanoic acid (sodium salt);

(ii) aliphatic, substituted aliphatic and arylalkyl monoperoxy acids, e.g. peroxyauric acid, peroxysearic acid, N-nonylamino-peroxycaproic acid (NAPCA), N,N-(3-octylsuccinoyl)aminoperoxyacproic acid (SAPA) and N,N-phthaloylaminoperoxyacproic acid (PAP);

(iii) amidoperoxyacids, e.g. monononylamide of either peroxysuccinic acid (NAPSA) or of peroxyadipic acid (NAPAA).

Typical diperoxyacids useful herein include alkyl diperoxyacids and aryldiperoxyacids, such as:

(iv) 1,12-diperoxydodecanedioic acid;

(v) 1,9-diperoxyazelaic acid;

(vi) diperoxybrassylic acid; diperoxysebacic acid and diperoxyisophthalic acid;

(vii) 2-decyldiperoxybutane-1,4-dioic acid;

(viii) 4,4'-sulfonylbisperoxybenzoic acid.

Such bleaching agents are disclosed in U.S. Patent 4,483,781, Hartman, issued November 20, 1984, U.S. Patent 4,634,551 to Burns et al., European Patent Application 0,133,354, Banks et al. published February 20, 1985, and U.S. Patent 4,412,934, Chung et al. issued November 1, 1983. Sources also include 6-nonylamino-6-oxoperoxyacproic acid as fully described in U.S. Patent 4,634,551, issued January 6, 1987 to Burns et al. Persulfate compounds such as for example OXONE, manufactured commercially by E.I. DuPont de Nemours of Wilmington, DE can also be employed as a suitable source of peroxymonosulfuric acid.

b. Hydrogen Peroxide Sources - The hydrogen peroxide source may be any suitable hydrogen peroxide source and present at such levels as fully described in U.S. Patent No. 5,576,282. For example, the hydrogen peroxide source may be selected from the group consisting

of perborate compounds, percarbonate compounds, perphosphate compounds and mixtures thereof.

Hydrogen peroxide sources are described in detail in the herein incorporated Kirk Othmer's Encyclopedia of Chemical Technology, 4th Ed (1992, John Wiley & Sons), Vol. 4, pp. 271-300 "Bleaching Agents (Survey)", and include the various forms of sodium perborate and sodium percarbonate, including various coated and modified forms.

The preferred source of hydrogen peroxide used herein can be any convenient source, including hydrogen peroxide itself. For example, perborate, e.g., sodium perborate (any hydrate but preferably the mono- or tetra-hydrate), sodium carbonate peroxyhydrate or equivalent percarbonate salts, sodium pyrophosphate peroxyhydrate, urea peroxyhydrate, or sodium peroxide can be used herein. Also useful are sources of available oxygen such as persulfate bleach (e.g., OXONE, manufactured by DuPont). Sodium perborate monohydrate and sodium percarbonate are particularly preferred. Mixtures of any convenient hydrogen peroxide sources can also be used.

A preferred percarbonate bleach comprises dry particles having an average particle size in the range from about 500 micrometers to about 1,000 micrometers, not more than about 10% by weight of said particles being smaller than about 200 micrometers and not more than about 10% by weight of said particles being larger than about 1,250 micrometers. Optionally, the percarbonate can be coated with a silicate, borate or water-soluble surfactants. Percarbonate is available from various commercial sources such as FMC, Solvay and Tokai Denka.

Compositions of the present invention may also comprise as the bleaching agent a chlorine-type bleaching material. Such agents are well known in the art, and include for example sodium dichloroisocyanurate ("NaDCC"). However, chlorine-type bleaches are less preferred for compositions which comprise enzymes.

b. Bleach Activators - Preferably, the peroxygen source in the composition is formulated with an activator (peracid precursor). The activator is present at levels of from about 0.01%, preferably from about 0.5%, more preferably from about 1% to about 15%, preferably to about 10%, more preferably to about 8%, by weight of the composition. A bleach activator as used herein is any compound which when used in conjunction with a hydrogen peroxide source leads to the in situ production of the peracid corresponding to the bleach activator. Various non limiting examples of activators are fully disclosed in U.S. Patent No. 5,576,282, U.S. Patent 4,915,854 and U.S. Patent 4,412,934. See also U.S. 4,634,551 for other typical bleaches and activators useful herein.

Preferred activators are selected from the group consisting of tetraacetyl ethylene diamine (TAED), benzoylcaprolactam (BzCL), 4-nitrobenzoylcaprolactam, 3-chlorobenzoylcaprolactam, benzoyloxybenzenesulphonate (BOBS), nonanoyloxybenzenesulphonate (NOBS), phenyl

benzoate (PhBz), decanoyloxybenzenesulphonate (C<sub>10</sub>-OBS), benzoylvalerolactam (BZVL), octanoyloxybenzenesulphonate (C<sub>8</sub>-OBS), perhydrolyzable esters and mixtures thereof, most preferably benzoylcaprolactam and benzoylvalerolactam. Particularly preferred bleach activators in the pH range from about 8 to about 9.5 are those selected having an OBS or VL leaving group.

5 Preferred hydrophobic bleach activators include, but are not limited to, nonanoyloxybenzenesulphonate (NOBS), 4-[N-(nonaoyl) amino hexanoyloxy]-benzene sulfonate sodium salt (NACA-OBS) an example of which is described in U.S. Patent No. 5,523,434, lauroyloxybenzenesulphonate (LOBS or C<sub>12</sub>-OBS), 10-undecenoyloxybenzenesulfonate (UDOBS or C<sub>11</sub>-OBS with unsaturation in the 10 position), and decanoyloxybenzoic acid (DOBA).

10 Preferred bleach activators are those described in U.S. 5,698,504 Christie et al., issued December 16, 1997; U.S. 5,695,679 Christie et al. issued December 9, 1997; U.S. 5,686,401 Willey et al., issued November 11, 1997; U.S. 5,686,014 Hartshorn et al., issued November 11, 1997; U.S. 5,405,412 Willey et al., issued April 11, 1995; U.S. 5,405,413 Willey et al., issued April 11, 1995; U.S. 5,130,045 Mitchel et al., issued July 14, 1992; and U.S. 4,412,934 Chung et al., issued November 1, 1983, and copending patent applications U. S. Serial Nos. 08/709,072, 15 08/064,564, all of which are incorporated herein by reference.

The mole ratio of peroxygen bleaching compound (as AvO) to bleach activator in the present invention generally ranges from at least 1:1, preferably from about 20:1, more preferably from about 10:1 to about 1:1, preferably to about 3:1.

20 Quaternary substituted bleach activators may also be included. The present bleaching compositions preferably comprise a quaternary substituted bleach activator (QSBA) or a quaternary substituted peracid (QSP); more preferably, the former. Preferred QSBA structures are further described in U.S. 5,686,015 Willey et al., issued November 11, 1997; U.S. 5,654,421 Taylor et al., issued August 5, 1997; U.S. 5,460,747 Gosselink et al., issued October 24, 1995; 25 U.S. 5,584,888 Miracle et al., issued December 17, 1996; and U.S. 5,578,136 Taylor et al., issued November 26, 1996; all of which are incorporated herein by reference.

Highly preferred bleach activators useful herein are amide-substituted as described in U.S. 5,698,504, U.S. 5,695,679, and U.S. 5,686,014 each of which are cited herein above. Preferred examples of such bleach activators include: (6-octanamidocaproyl) 30 oxybenzenesulfonate, (6-nonanamidocaproyl)oxybenzenesulfonate, (6-decanamido caproyl)oxybenzenesulfonate and mixtures thereof.

Other useful activators, disclosed in U.S. 5,698,504, U.S. 5,695,679, U.S. 5,686,014 each of which is cited herein above and U.S. 4,966,723Hodge et al., issued October 30, 1990, include benzoxazin-type activators, such as a C<sub>6</sub>H<sub>4</sub> ring to which is fused in the 1,2-positions a moiety -- 35 C(O)OC(R<sup>1</sup>)=N-.

Depending on the activator and precise application, good bleaching results can be obtained from bleaching systems having with in-use pH of from about 6 to about 13, preferably from about 9.0 to about 10.5. Typically, for example, activators with electron-withdrawing moieties are used for near-neutral or sub-neutral pH ranges. Alkalis and buffering agents can be used to secure such pH.

Acyl lactam activators, as described in U.S. 5,698,504, U.S. 5,695,679 and U.S. 5,686,014, each of which is cited herein above, are very useful herein, especially the acyl caprolactams (see for example WO 94-28102 A) and acyl valerolactams (see U.S. 5,503,639 Willey et al., issued April 2, 1996 incorporated herein by reference).

d. Organic Peroxides, especially Diacyl Peroxides - In addition to the bleaching agents described above, the bleaching compositions of the present invention can optionally include organic peroxides. Organic peroxide are extensively illustrated in Kirk Othmer, Encyclopedia of Chemical Technology, Vol. 17, John Wiley and Sons, 1982 at pages 27-90 and especially at pages 63-72, all incorporated herein by reference. If a diacyl peroxide is used, it will preferably be one which exerts minimal adverse impact on spotting/filming.

e. Metal-containing Bleach Catalysts - The bleaching compositions can also optionally include metal-containing bleach catalysts, preferably manganese and cobalt-containing bleach catalysts.

One type of metal-containing bleach catalyst is a catalyst system comprising a transition metal cation of defined bleach catalytic activity, such as copper, iron, titanium, ruthenium tungsten, molybdenum, or manganese cations, an auxiliary metal cation having little or no bleach catalytic activity, such as zinc or aluminum cations, and a sequester having defined stability constants for the catalytic and auxiliary metal cations, particularly ethylenediaminetetraacetic acid, ethylenediaminetetra (methylenephosphonic acid) and water-soluble salts thereof. Such catalysts are disclosed in U.S. 4,430,243 Bragg, issued February 2, 1982.

i. Manganese Metal Complexes - If desired, the compositions herein can be catalyzed by means of a manganese compound. Such compounds and levels of use are well known in the art and include, for example, the manganese-based catalysts disclosed in U.S. 5,576,282 Miracle et al., issued November 19, 1996; U.S. 5,246,621 Favre et al., issued September 21, 1993; U.S. 5,244,594 Favre et al., issued September 14, 1993; U.S. 5,194,416 Jureller et al., issued March 16, 1993; U.S. 5,114,606 van Vliet et al., issued May 19, 1992; and European Pat. App. Pub. Nos. 549,271 A1, 549,272 A1, 544,440 A2, and 544,490 A1; Preferred examples of these catalysts include  $\text{Mn}^{\text{IV}}_2(\text{u-O})_3(1,4,7\text{-trimethyl-1,4,7-triazacyclononane})_2(\text{PF}_6)_2$ ,  $\text{Mn}^{\text{III}}_2(\text{u-O})_1(\text{u-OAc})_2(1,4,7\text{-trimethyl-1,4,7-triazacyclononane})_2(\text{ClO}_4)_2$ ,  $\text{Mn}^{\text{IV}}_4(\text{u-O})_6(1,4,7\text{-triazacyclononane})_4(\text{ClO}_4)_4$ ,  $\text{Mn}^{\text{III}}\text{Mn}^{\text{IV}}_4(\text{u-O})_1(\text{u-OAc})_2(1,4,7\text{-trimethyl-1,4,7-}$

triazacyclononane)<sub>2</sub>(ClO<sub>4</sub>)<sub>3</sub>, Mn<sup>IV</sup>(1,4,7-trimethyl-1,4,7-triazacyclononane)-(OCH<sub>3</sub>)<sub>3</sub>(PF<sub>6</sub>), and mixtures thereof. Other metal-based bleach catalysts include those disclosed in U.S. 4,430,243 included by reference herein above and U.S. 5,114,611 van Kralingen, issued May 19, 1992. The use of manganese with various complex ligands to enhance bleaching is also reported in the following: U.S. 4,728,455 Rerek, issued March 1, 1988; U.S. 5,284,944 Madison, issued February 8, 1994; U.S. 5,246,612 van Dijk et al., issued September 21, 1993; U.S. 5,256,779 Kerschner et al., issued October 26, 1993; U.S. 5,280,117 Kerschner et al., issued January 18, 1994; U.S. 5,274,147 Kerschner et al., issued December 28, 1993; U.S. 5,153,161 Kerschner et al., issued October 6, 1992; and U.S. 5,227,084 Martens et al., issued July 13, 1993.

- 10           ii. Cobalt Metal Complexes - Cobalt bleach catalysts useful herein are known, and are described, for example, in U.S. 5,597,936 Perkins et al., issued January 28, 1997; U.S. 5,595,967 Miracle et al., January 21, 1997; U.S. 5,703,030 Perkins et al., issued December 30, 1997; and M. L. Tobe, "Base Hydrolysis of Transition-Metal Complexes", Adv. Inorg. Bioinorg. Mech., (1983), 2, pages 1-94. The most preferred cobalt catalyst useful herein are cobalt pentaamine acetate salts having the formula [Co(NH<sub>3</sub>)<sub>5</sub>OAc] T<sub>y</sub>, wherein "OAc" represents an acetate moiety and "T<sub>y</sub>" is an anion, and especially cobalt pentaamine acetate chloride, [Co(NH<sub>3</sub>)<sub>5</sub>OAc]Cl<sub>2</sub>; as well as [Co(NH<sub>3</sub>)<sub>5</sub>OAc](OAc)<sub>2</sub>; [Co(NH<sub>3</sub>)<sub>5</sub>OAc](PF<sub>6</sub>)<sub>2</sub>; [Co(NH<sub>3</sub>)<sub>5</sub>OAc](SO<sub>4</sub>); [Co(NH<sub>3</sub>)<sub>5</sub>OAc](BF<sub>4</sub>)<sub>2</sub>; and [Co(NH<sub>3</sub>)<sub>5</sub>OAc](NO<sub>3</sub>)<sub>2</sub> (herein "PAC").

20           These cobalt catalysts are readily prepared by known procedures, such as taught for example in U.S. 5,597,936, U.S. 5,595,967, U.S. 5,703,030, cited herein above, the Tobe article and the references cited therein, and in U.S. Patent 4,810,410, to Diakun et al, issued March 7, 1989, J. Chem. Ed. (1989), 66 (12), 1043-45; The Synthesis and Characterization of Inorganic Compounds, W.L. Jolly (Prentice-Hall; 1970), pp. 461-3; Inorg. Chem., 18, 1497-1502 (1979); Inorg. Chem., 21, 2881-2885 (1982); Inorg. Chem., 18, 2023-2025 (1979); Inorg. Synthesis, 173-176 (1960); and Journal of Physical Chemistry, 56, 22-25 (1952).

- 25           iii. Transition Metal Complexes of Macropolycyclic Rigid Ligands - Compositions herein may also suitably include as bleach catalyst a transition metal complex of a macropolycyclic rigid ligand. The phrase "macropolycyclic rigid ligand" is sometimes abbreviated as "MRL" in discussion below. The amount used is a catalytically effective amount, suitably about 30 1 ppb or more, for example up to about 99.9%, more typically about 0.001 ppm or more, preferably from about 0.05 ppm to about 500 ppm (wherein "ppb" denotes parts per billion by weight and "ppm" denotes parts per million by weight).

35           Suitable transition metals e.g., Mn are illustrated hereinafter. "Macropolycyclic" means a MRL is both a macrocycle and is polycyclic. "Polycyclic" means at least bicyclic. The term "rigid" as used herein herein includes "having a superstructure" and "cross-bridged". "Rigid" has

been defined as the constrained converse of flexibility: see D.H. Busch., Chemical Reviews., (1993), 93, 847-860, incorporated by reference. More particularly, "rigid" as used herein means that the MRL must be determinably more rigid than a macrocycle ("parent macrocycle") which is otherwise identical (having the same ring size and type and number of atoms in the main ring) but lacking a superstructure (especially linking moieties or, preferably cross-bridging moieties) found in the MRL's. In determining the comparative rigidity of macrocycles with and without superstructures, the practitioner will use the free form (not the metal-bound form) of the macrocycles. Rigidity is well-known to be useful in comparing macrocycles; suitable tools for determining, measuring or comparing rigidity include computational methods (see, for example, Zimmer, Chemical Reviews., (1995), 95(38), 2629-2648 or Hancock et al., Inorganica Chimica Acta, (1989), 164, 73-84.

Preferred MRL's herein are a special type of ultra-rigid ligand which is cross-bridged. A "cross-bridge" is nonlimitingly illustrated in 1.11 hereinbelow. In 1.11, the cross-bridge is a -CH<sub>2</sub>CH<sub>2</sub>- moiety. It bridges N<sup>1</sup> and N<sup>8</sup> in the illustrative structure. By comparison, a "same-side" bridge, for example if one were to be introduced across N<sup>1</sup> and N<sup>12</sup> in 1.11, would not be sufficient to constitute a "cross-bridge" and accordingly would not be preferred.

Suitable metals in the rigid ligand complexes include Mn(II), Mn(III), Mn(IV), Mn(V), Fe(II), Fe(III), Fe(IV), Co(I), Co(II), Co(III), Ni(I), Ni(II), Ni(III), Cu(I), Cu(II), Cu(III), Cr(II), Cr(III), Cr(IV), Cr(V), Cr(VI), V(III), V(IV), V(V), Mo(IV), Mo(V), Mo(VI), W(IV), W(V), W(VI), Pd(II), Ru(II), Ru(III), and Ru(IV). Preferred transition-metals in the instant transition-metal bleach catalyst include manganese, iron and chromium.

More generally, the MRL's (and the corresponding transition-metal catalysts) herein suitably comprise:

- (a) at least one macrocycle main ring comprising four or more heteroatoms; and
- (b) a covalently connected non-metal superstructure capable of increasing the rigidity of the macrocycle, preferably selected from
  - (i) a bridging superstructure, such as a linking moiety;
  - (ii) a cross-bridging superstructure, such as a cross-bridging linking moiety; and
  - (iii) combinations thereof.

The term "superstructure" is used herein as defined in the literature by Busch et al., see, for example, articles by Busch in "Chemical Reviews".

Preferred superstructures herein not only enhance the rigidity of the parent macrocycle, but also favor folding of the macrocycle so that it co-ordinates to a metal in a cleft. Suitable superstructures can be remarkably simple, for example a linking moiety such as any of those illustrated in Fig. 1 and Fig. 2 below, can be used.

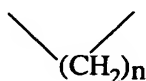


Fig. 1

wherein n is an integer, for example from 2 to 8, preferably less than 6, typically 2 to 4, or

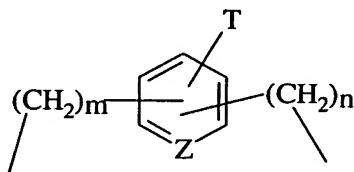


Fig. 2

wherein m and n are integers from about 1 to 8, more preferably from 1 to 3; Z is N or CH; and T is a compatible substituent, for example H, alkyl, trialkylammonium, halogen, nitro, sulfonate, or the like. The aromatic ring in 1.10 can be replaced by a saturated ring, in which the atom in Z connecting into the ring can contain N, O, S or C.

Suitable MRL's are further nonlimitingly illustrated by the following compound:

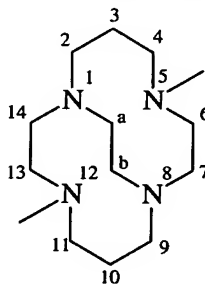


Fig. 3

This is a MRL in accordance with the invention which is a highly preferred, cross-bridged, methyl-substituted (all nitrogen atoms tertiary) derivative of cyclam. Formally, this ligand is named 5,12-dimethyl-1,5,8,12-tetraazabicyclo[6.6.2]hexadecane using the extended von Baeyer system. See "A Guide to IUPAC Nomenclature of Organic Compounds: Recommendations 1993", R. Panico, W.H. Powell and J-C Richer (Eds.), Blackwell Scientific Publications, Boston, 1993; see especially section R-2.4.2.1.

Transition-metal bleach catalysts of Macrocyclic Rigid Ligands which are suitable for use in the invention compositions can in general include known compounds where they conform with the definition herein, as well as, more preferably, any of a large number of novel compounds expressly designed for the present laundry or cleaning uses, and non-limitingly illustrated by any of the following:

Dichloro-5,12-dimethyl-1,5,8,12-tetraazabicyclo[6.6.2]hexadecane Manganese(II)

Diaquo-5,12-dimethyl-1,5,8,12-tetraazabicyclo[6.6.2]hexadecane Manganese(II)

Hexafluorophosphate

Aquo-hydroxy-5,12-dimethyl-1,5,8,12-tetraazabicyclo[6.6.2]hexadecane Manganese(III)

Hexafluorophosphate

Diaquo-5,12-dimethyl-1,5,8,12-tetraazabicyclo[6.6.2]hexadecane Manganese(II)

5 Tetrafluoroborate

Dichloro-5,12-dimethyl-1,5,8,12-tetraazabicyclo[6.6.2]hexadecane Manganese(III)

Hexafluorophosphate

Dichloro-5,12-di-n-butyl-1,5,8,12-tetraaza bicyclo[6.6.2]hexadecane Manganese(II)

Dichloro-5,12-dibenzyl-1,5,8,12-tetraazabicyclo[6.6.2]hexadecane Manganese(II)

10 Dichloro-5-n-butyl-12-methyl-1,5,8,12-tetraaza- bicyclo[6.6.2]hexadecane Manganese(II)

Dichloro-5-n-octyl-12-methyl-1,5,8,12-tetraaza- bicyclo[6.6.2]hexadecane Manganese(II)

Dichloro-5-n-butyl-12-methyl-1,5,8,12-tetraaza- bicyclo[6.6.2]hexadecane Manganese(II).

As a practical matter, and not by way of limitation, the compositions and cleaning processes herein can be adjusted to provide on the order of at least one part per hundred million of the active bleach catalyst species in the aqueous washing medium, and will preferably provide from about 0.01 ppm to about 25 ppm, more preferably from about 0.05 ppm to about 10 ppm, and most preferably from about 0.1 ppm to about 5 ppm, of the bleach catalyst species in the wash liquor. In order to obtain such levels in the wash liquor of an automatic washing process, typical compositions herein will comprise from about 0.0005% to about 0.2%, more preferably from about 0.004% to about 0.08%, of bleach catalyst, especially manganese or cobalt catalysts, by weight of the cleaning compositions.

Preferably, the peroxygen source is selected from hydrogen peroxide sources selected from the group consisting of perborate compounds, percarbonate compounds, perphosphate compounds and mixtures thereof, and a bleach activator.

Preferably, the bleach activator is selected from the group consisting of hydrophobic bleach activators as disclosed herein.

The purpose of such a bleaching composition is to mitigate unwanted decomposition of the organic catalyst.

Bleaching Agents - The compositions of the present invention optionally comprise, in addition to the bleaching system described above, additional bleaching agents, such as chlorine bleaches (although less preferred for compositions which comprise enzymes) examples of which are known in the art, and include sodium dichloroisocyanurate ("NaDCC) and bleach catalysts. When present, these other bleaching agents will typically be at levels of from about 1%, preferably from about 5% to about 30%, preferably to about 20% by weight of the composition.



(a) Organic Peroxides, especially Diacyl Peroxides - These are extensively illustrated in Kirk Othmer, Encyclopedia of Chemical Technology, Vol. 17, John Wiley and Sons, 1982 at pages 27-90 and especially at pages 63-72, all incorporated herein by reference. If a diacyl peroxide is used, it will preferably be one which exerts minimal adverse impact on spotting/filming.

(b) Metal-containing Bleach Catalysts - The present invention compositions and methods may utilize metal-containing bleach catalysts that are effective for use in bleaching compositions. Preferred are manganese and cobalt-containing bleach catalysts.

One type of metal-containing bleach catalyst is a catalyst system comprising a transition metal cation of defined bleach catalytic activity, such as copper, iron, titanium, ruthenium, tungsten, molybdenum, or manganese cations, an auxiliary metal cation having little or no bleach catalytic activity, such as zinc or aluminum cations, and a sequester having defined stability constants for the catalytic and auxiliary metal cations, particularly ethylenediaminetetraacetic acid, ethylenediaminetetra (methylenephosphonic acid) and water-soluble salts thereof. Such catalysts are disclosed in U.S. 4,430,243 Bragg, issued February 2, 1982.

Manganese Metal Complexes - If desired, the compositions herein can be catalyzed by means of a manganese compound. Such compounds and levels of use are well known in the art and include, for example, the manganese-based catalysts disclosed in U.S. Patent Nos. 5,576,282; 5,246,621; 5,244,594; 5,194,416; and 5,114,606; and European Pat. App. Pub. Nos. 549,271 A1, 549,272 A1, 544,440 A2, and 544,490 A1; Preferred examples of these catalysts include  $\text{Mn}^{\text{IV}}_2(\text{u-O})_3(1,4,7\text{-trimethyl-1,4,7-triazacyclononane})_2(\text{PF}_6)_2$ ,  $\text{Mn}^{\text{III}}_2(\text{u-O})_1(\text{u-OAc})_2(1,4,7\text{-trimethyl-1,4,7-triazacyclononane})_2(\text{ClO}_4)_2$ ,  $\text{Mn}^{\text{IV}}_4(\text{u-O})_6(1,4,7\text{-triazacyclononane})_4(\text{ClO}_4)_4$ ,  $\text{Mn}^{\text{III}}\text{Mn}^{\text{IV}}_4(\text{u-O})_1(\text{u-OAc})_2(1,4,7\text{-trimethyl-1,4,7-triazacyclononane})_2(\text{ClO}_4)_3$ ,  $\text{Mn}^{\text{IV}}(1,4,7\text{-trimethyl-1,4,7-triazacyclononane})-(\text{OCH}_3)_3(\text{PF}_6)$ , and mixtures thereof. Other metal-based bleach catalysts include those disclosed in U.S. Patent Nos. 4,430,243 and U.S. 5,114,611. The use of manganese with various complex ligands to enhance bleaching is also reported in the following: U.S. Patent Nos. 4,728,455; 5,284,944; 5,246,612; 5,256,779; 5,280,117; 5,274,147; 5,153,161; and 5,227,084.

Cobalt Metal Complexes - Cobalt bleach catalysts useful herein are known, and are described, for example, in U.S. Patent Nos. 5,597,936; 5,595,967; and 5,703,030; and M. L. Tobe, "Base Hydrolysis of Transition-Metal Complexes", Adv. Inorg. Bioinorg. Mech., (1983), 2, pages 1-94. The most preferred cobalt catalyst useful herein are cobalt pentaamine acetate salts having the formula  $[\text{Co}(\text{NH}_3)_5\text{OAc}] \text{T}_y$ , wherein "OAc" represents an acetate moiety and "T<sub>y</sub>" is an anion, and especially cobalt pentaamine acetate chloride,  $[\text{Co}(\text{NH}_3)_5\text{OAc}]\text{Cl}_2$ ; as well as

[Co(NH<sub>3</sub>)<sub>5</sub>OAc](OAc)<sub>2</sub>; [Co(NH<sub>3</sub>)<sub>5</sub>OAc](PF<sub>6</sub>)<sub>2</sub>; [Co(NH<sub>3</sub>)<sub>5</sub>OAc](SO<sub>4</sub>); [Co(NH<sub>3</sub>)<sub>5</sub>OAc](BF<sub>4</sub>)<sub>2</sub>; and [Co(NH<sub>3</sub>)<sub>5</sub>OAc](NO<sub>3</sub>)<sub>2</sub> (herein "PAC").

These cobalt catalysts are readily prepared by known procedures, such as taught for example in U.S. Patent Nos. 5,597,936; 5,595,967; and 5,703,030; in the Tobe article and the references cited therein; and in U.S. Patent 4,810,410; J. Chem. Ed. (1989), 66 (12), 1043-45; The Synthesis and Characterization of Inorganic Compounds, W.L. Jolly (Prentice-Hall; 1970), pp. 461-3; Inorg. Chem., 18, 1497-1502 (1979); Inorg. Chem., 21, 2881-2885 (1982); Inorg. Chem., 18, 2023-2025 (1979); Inorg. Synthesis, 173-176 (1960); and Journal of Physical Chemistry, 56, 22-25 (1952).

Transition Metal Complexes of Macropolycyclic Rigid Ligands - Compositions herein may also suitably include as bleach catalyst a transition metal complex of a macropolycyclic rigid ligand. The phrase "macropolycyclic rigid ligand" is sometimes abbreviated as "MRL" in discussion below. The amount used is a catalytically effective amount, suitably about 1 ppb or more, for example up to about 99.9%, more typically about 0.001 ppm or more, preferably from about 0.05 ppm to about 500 ppm (wherein "ppb" denotes parts per billion by weight and "ppm" denotes parts per million by weight).

Suitable transition metals e.g., Mn are illustrated hereinafter. "Macropolycyclic" means a MRL is both a macrocycle and is polycyclic. "Polycyclic" means at least bicyclic. The term "rigid" as used herein herein includes "having a superstructure" and "cross-bridged". "Rigid" has been defined as the constrained converse of flexibility: see D.H. Busch., Chemical Reviews., (1993), 93, 847-860, incorporated by reference. More particularly, "rigid" as used herein means that the MRL must be determinably more rigid than a macrocycle ("parent macrocycle") which is otherwise identical (having the same ring size and type and number of atoms in the main ring) but lacking a superstructure (especially linking moieties or, preferably cross-bridging moieties) found in the MRL's. In determining the comparative rigidity of macrocycles with and without superstructures, the practitioner will use the free form (not the metal-bound form) of the macrocycles. Rigidity is well-known to be useful in comparing macrocycles; suitable tools for determining, measuring or comparing rigidity include computational methods (see, for example, Zimmer, Chemical Reviews., (1995), 95(38), 2629-2648 or Hancock et al., Inorganica Chimica Acta, (1989), 164, 73-84.

Preferred MRL's herein are a special type of ultra-rigid ligand which is cross-bridged. A "cross-bridge" is nonlimitingly illustrated in 1.11 hereinbelow. In 1.11, the cross-bridge is a -CH<sub>2</sub>CH<sub>2</sub>- moiety. It bridges N<sup>1</sup> and N<sup>8</sup> in the illustrative structure. By comparison, a "same-side" bridge, for example if one were to be introduced across N<sup>1</sup> and N<sup>12</sup> in 1.11, would not be sufficient to constitute a "cross-bridge" and accordingly would not be preferred.

Suitable metals in the rigid ligand complexes include Mn(II), Mn(III), Mn(IV), Mn(V), Fe(II), Fe(III), Fe(IV), Co(I), Co(II), Co(III), Ni(I), Ni(II), Ni(III), Cu(I), Cu(II), Cu(III), Cr(II), Cr(III), Cr(IV), Cr(V), Cr(VI), V(III), V(IV), V(V), Mo(IV), Mo(V), Mo(VI), W(IV), W(V), W(VI), Pd(II), Ru(II), Ru(III), and Ru(IV). Preferred transition-metals in the instant transition-metal bleach catalyst include manganese, iron and chromium.

More generally, the MRL's (and the corresponding transition-metal catalysts) herein suitably comprise:

- (a) at least one macrocycle main ring comprising four or more heteroatoms; and
- (b) a covalently connected non-metal superstructure capable of increasing the rigidity of the macrocycle, preferably selected from
  - (i) a bridging superstructure, such as a linking moiety;
  - (ii) a cross-bridging superstructure, such as a cross-bridging linking moiety; and
  - (iii) combinations thereof.

The term "superstructure" is used herein as defined in the literature by Busch et al., see, for example, articles by Busch in "Chemical Reviews".

Preferred superstructures herein not only enhance the rigidity of the parent macrocycle, but also favor folding of the macrocycle so that it co-ordinates to a metal in a cleft. Suitable superstructures can be remarkably simple, for example a linking moiety such as any of those illustrated in Fig. 1 and Fig. 2 below, can be used.

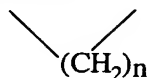


Fig. 1

wherein n is an integer, for example from 2 to 8, preferably less than 6, typically 2 to 4, or

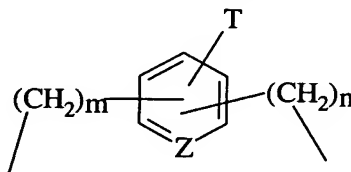


Fig. 2

wherein m and n are integers from about 1 to 8, more preferably from 1 to 3; Z is N or CH; and T is a compatible substituent, for example H, alkyl, trialkylammonium, halogen, nitro, sulfonate, or the like. The aromatic ring in 1.10 can be replaced by a saturated ring, in which the atom in Z connecting into the ring can contain N, O, S or C.

Suitable MRL's are further nonlimitingly illustrated by the following compound:

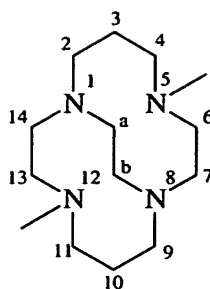


Fig. 3

This is a MRL in accordance with the invention which is a highly preferred, cross-bridged, methyl-substituted (all nitrogen atoms tertiary) derivative of cyclam. Formally, this ligand is named 5,12-dimethyl-1,5,8,12-tetraazabicyclo[6.6.2]hexadecane using the extended von Baeyer system. See "A Guide to IUPAC Nomenclature of Organic Compounds: Recommendations 1993", R. Panico, W.H. Powell and J-C Richer (Eds.), Blackwell Scientific Publications, Boston, 1993; see especially section R-2.4.2.1.

Transition-metal bleach catalysts of Macrocyclic Rigid Ligands which are suitable for use in the invention compositions can in general include known compounds where they conform with the definition herein, as well as, more preferably, any of a large number of novel compounds expressly designed for the present laundry or cleaning uses, and non-limitingly illustrated by any of the following:

Dichloro-5,12-dimethyl-1,5,8,12-tetraazabicyclo[6.6.2]hexadecane Manganese(II)

Diaquo-5,12-dimethyl-1,5,8,12-tetraazabicyclo[6.6.2]hexadecane Manganese(II) Hexafluorophosphate  
Aquo-hydroxy-5,12-dimethyl-1,5,8,12-tetraazabicyclo[6.6.2]hexadecane Manganese(III)

Hexafluorophosphate

Diaquo-5,12-dimethyl-1,5,8,12-tetraazabicyclo[6.6.2]hexadecane Manganese(II) Tetrafluoroborate

Dichloro-5,12-dimethyl-1,5,8,12-tetraazabicyclo[6.6.2]hexadecane Manganese(III)

Hexafluorophosphate

Dichloro-5,12-di-n-butyl-1,5,8,12-tetraaza bicyclo[6.6.2]hexadecane Manganese(II)

Dichloro-5,12-dibenzyl-1,5,8,12-tetraazabicyclo[6.6.2]hexadecane Manganese(II)

Dichloro-5-n-butyl-12-methyl-1,5,8,12-tetraaza- bicyclo[6.6.2]hexadecane Manganese(II)

Dichloro-5-n-octyl-12-methyl-1,5,8,12-tetraaza- bicyclo[6.6.2]hexadecane Manganese(II)

Dichloro-5-n-butyl-12-methyl-1,5,8,12-tetraaza- bicyclo[6.6.2]hexadecane Manganese(II).

As a practical matter, and not by way of limitation, the compositions and cleaning processes herein can be adjusted to provide on the order of at least one part per hundred million of the active bleach catalyst species in the aqueous washing medium, and will preferably provide from about 0.01 ppm to about 25 ppm, more preferably from about 0.05 ppm to about 10 ppm, and

most preferably from about 0.1 ppm to about 5 ppm, of the bleach catalyst species in the wash liquor. In order to obtain such levels in the wash liquor of an automatic washing process, typical compositions herein will comprise from about 0.0005% to about 0.2%, more preferably from about 0.004% to about 0.08%, of bleach catalyst, especially manganese or cobalt catalysts, by weight of the bleaching compositions.

(d) Other Bleach Catalysts - The compositions herein may comprise one or more other bleach catalysts. Preferred bleach catalysts are zwitterionic bleach catalysts, which are described in U.S. Patent No. 5,576,282 (especially 3-(3,4-dihydroisoquinolinium) propane sulfonate. Other bleach catalysts include cationic bleach catalysts are described in U.S. Patent Nos. 5,360,569, 5,442,066, 5,478,357, 5,370,826, 5,482,515, 5,550,256, and WO 95/13351, WO 95/13352, and WO 95/13353.

Enzymes - The bleaching compositions can comprise one or more detergent enzymes which provide cleaning performance and/or fabric care benefits. Such enzymes can include proteases, amylases, cellulases and lipases. They may be incorporated into the non-aqueous liquid bleaching compositions herein in the form of suspensions, "marumes" or "prills". Another suitable type of enzyme comprises those in the form of slurries of enzymes in nonionic surfactants, e.g., the enzymes marketed by Novo Nordisk under the tradename "SL" or the microencapsulated enzymes marketed by Novo Nordisk under the tradename "LDP." Suitable enzymes and levels of use are described in U.S. Pat. Nos. 5,705,464, 5,710,115, 5,576,282, 5,728,671 and 5,707,950.

Enzymes added to the compositions herein in the form of conventional enzyme prills are especially preferred for use herein. Such prills will generally range in size from about 100 to 1,000 microns, more preferably from about 200 to 800 microns and will be suspended throughout the non-aqueous liquid phase of the composition. Prills in the compositions of the present invention have been found, in comparison with other enzyme forms, to exhibit especially desirable enzyme stability in terms of retention of enzymatic activity over time. Thus, compositions which utilize enzyme prills need not contain conventional enzyme stabilizing such as must frequently be used when enzymes are incorporated into aqueous liquid detergents.

However, enzymes added to the compositions herein may be in the form of granulates, preferably T-granulates. successive improvements, have a remaining degree of bleach deactivation susceptibility.

Examples of suitable enzymes include, but are not limited to, hemicellulases, peroxidases, proteases, cellulases, xylanases, lipases, phospholipases, esterases, cutinases, pectinases, keratanases, reductases, oxidases, phenoloxidases, lipoxxygenases, ligninases, pullulanases, tannases, pentosanases, malanases,  $\beta$ glucanases, arabinosidases, hyaluronidase, chondroitinase, laccase, mannanases, more preferably plant cell wall degrading enzymes and non-cell wall-

degrading enzymes (WO 98/39403 A) and can, more specifically, include pectinase (WO 98/06808 A, JP10088472 A, JP10088485 A); pectolyase (WO98/06805 A1); pectin lyases free from other pectic enzymes (WO9806807 A1); chondriotinase (EP 747,469 A); xylanase (EP 709,452 A, WO 98/39404 A, WO98/39402 A) including those derived from *microtetraspora flexuosa* (US 5683911); isopeptidase (WO 98/16604 A); keratinase (EP 747,470 A, WO 98/40473 A); lipase (GB 2,297,979 A; WO 96/16153 A; WO 96/12004 A; EP 698,659 A; WO 96/16154 A); cellulase or endoglucanase (GB 2,294,269 A; WO 96/27649 A; GB 2,303,147 A; WO98/03640 A; see also neutral or alkaline cellulases derived from *chrysosporium lucknowense* strain VKM F-3500D as disclosed in WO9815633 A); polygalacturonase (WO 98/06809 A); mycodextranase (WO 98/13457 A); thermitase (WO 96/28558 A); cholesterol esterase (WO 98 28394 A); or any combination thereof; and known amylases; oxidoreductases; oxidases or combination systems including same (DE19523389 A1); mutant blue copper oxidases (WO9709431 A1), peroxidases (see for example US 5,605,832, WO97/31090 A1), mannanases (WO9711164, WO 99/09126, PCT/US00/00839); xyloglucanases (WO 98/50513, PCT/US/00/00839, WO 99/02663); laccases, see WO9838287 A1 or WO9838286 A1 or for example, those laccase variants having amino acid changes in *myceliophthora* or *scytalidium* laccase(s) as described in WO9827197 A1 or mediated laccase systems as described in DE19612193 A1), or those derived from *coprinus* strains (see, for example WO9810060 A1 or WO9827198 A1), phenol oxidase or polyphenol oxidase (JP10174583 A) or mediated phenol oxidase systems (WO9711217 A); enhanced phenol oxidase systems (WO 9725468 A WO9725469 A); phenol oxidases fused to an amino acid sequence having a cellulose binding domain (WO9740127 A1, WO9740229 A1) or other phenol oxidases (WO9708325 A, WO9728257 A1) or superoxide dismutases. Oxidoreductases and/or their associated antibodies can be used, for example with H<sub>2</sub>O<sub>2</sub>, as taught in WO 98/07816 A. Depending on the type of composition, other redox-active enzymes can be used, even, for example, catalases (see, for example JP09316490 A). A preferred combination is a bleaching composition having a cocktail of conventional applicable enzymes like protease, lipase, cutinase and/or cellulase in conjunction with the amylase of the present invention.

Suitable proteases are the subtilisins which are obtained from particular strains of *B. subtilis* and *B. licheniformis* (subtilisin BPN and BPN'). One suitable protease is obtained from a strain of *Bacillus*, having maximum activity throughout the pH range of 8-12, developed and sold as ESPERASE® by Novo Industries A/S of Denmark, hereinafter "Novo". The preparation of this enzyme and analogous enzymes is described in GB 1,243,784 to Novo. Other suitable proteases include ALCALASE®, DURAZYM® and SAVINASE® from Novo and MAXATASE®, MAXACAL®, PROPERASE® and MAXAPEM® (protein engineered Maxacal) from Gist-

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Brocades. Proteolytic enzymes also encompass modified bacterial serine proteases, such as those described in European Patent Application Serial Number 87 303761.8, filed April 28, 1987 (particularly pages 17, 24 and 98), and which is called herein "Protease B", and in European Patent Application 199,404, Venegas, published October 29, 1986, which refers to a modified bacterial serine proteolytic enzyme which is called "Protease A" herein. More preferred is what is called herein "Protease C", which is a variant of an alkaline serine protease from *Bacillus* in which lysine replaced arginine at position 27, tyrosine replaced valine at position 104, serine replaced asparagine at position 123, and alanine replaced threonine at position 274. Protease C is described in EP 90915958:4, corresponding to WO 91/06637, Published May 16, 1991. Genetically modified variants, particularly of Protease C, are also included herein. See also a high pH protease from *Bacillus* sp. NCIMB 40338 described in WO 93/18140 A to Novo. Enzymatic detergents comprising protease, one or more other enzymes, and a reversible protease inhibitor are described in WO 92/03529 A to Novo. When desired, a protease having decreased adsorption and increased hydrolysis is available as described in WO 95/07791 to Procter & Gamble. A recombinant trypsin-like protease for detergents suitable herein is described in WO 94/25583 to Novo.

In more detail, the protease referred to as "Protease D" is a carbonyl hydrolase variant having an amino acid sequence not found in nature, which is derived from a precursor carbonyl hydrolase by substituting a different amino acid for a plurality of amino acid residues at a position in said carbonyl hydrolase equivalent to position +76, preferably also in combination with one or more amino acid residue positions equivalent to those selected from the group consisting of +99, +101, +103, +104, +107, +123, +27, +105, +109, +126, +128, +135, +156, +166, +195, +197, +204, +206, +210, +216, +217, +218, +222, +260, +265, and/or +274 according to the numbering of *Bacillus amyloliquefaciens* subtilisin, as described in WO 95/10615 published April 20, 1995 by Genencor International. Also suitable for the present invention are proteases described in patent applications EP 251 446 and WO91/06637 and protease BLAP® described in WO91/02792. The proteolytic enzymes are incorporated in the bleaching compositions of the present invention a level of from 0.0001% to 2%, preferably from 0.001% to 0.2%, more preferably from 0.005% to 0.1% pure enzyme by weight of the composition.

Useful proteases are also described in PCT publications: WO 95/30010 published November 9, 1995 by The Procter & Gamble Company; WO 95/30011 published November 9, 1995 by The Procter & Gamble Company; WO 95/29979 published November 9, 1995 by The Procter & Gamble Company.

Other particularly useful proteases are multiply-substituted protease variants comprising a substitution of an amino acid residue with another naturally occurring amino acid residue at an amino acid residue position corresponding to position 103 of *Bacillus*

5 *amyloliquefaciens* subtilisin in combination with a substitution of an amino acid residue with another naturally occurring amino acid residue at one or more amino acid residue positions corresponding to positions 1, 3, 4, 8, 9, 10, 12, 13, 16, 17, 18, 19, 20, 21, 22, 24, 27, 33, 37, 38, 42, 43, 48, 55, 57, 58, 61, 62, 68, 72, 75, 76, 77, 78, 79, 86, 87, 89, 97, 98, 99, 101, 102, 104, 106, 107, 109, 111, 114, 116, 117, 119, 121, 123, 126, 128, 130, 131, 133, 134, 137, 140, 141, 142, 146, 147, 158, 159, 160, 166, 167, 170, 173, 174, 177, 181, 182, 183, 184, 185, 188, 192, 194, 198, 203, 204, 205, 206, 209, 210, 211, 212, 213, 214, 215, 216, 217, 218, 222, 224, 227, 228, 230, 232, 236, 237, 238, 240, 242, 243, 244, 245, 246, 247, 248, 249, 251, 252, 253, 254, 255, 256, 257, 258, 259, 260, 261, 262, 263, 265, 10 268, 269, 270, 271, 272, 274 and 275 of *Bacillus amyloliquefaciens* subtilisin; wherein when said protease variant includes a substitution of amino acid residues at positions corresponding to positions 103 and 76, there is also a substitution of an amino acid residue at one or more amino acid residue positions other than amino acid residue positions corresponding to positions 27, 99, 101, 104, 107, 109, 123, 128, 166, 204, 206, 15 210, 216, 217, 218, 222, 260, 265 or 274 of *Bacillus amyloliquefaciens* subtilisin and/or multiply-substituted protease variants comprising a substitution of an amino acid residue with another naturally occurring amino acid residue at one or more amino acid residue positions corresponding to positions 62, 212, 230, 232, 252 and 257 of *Bacillus amyloliquefaciens* subtilisin as described in PCT Patent Publication Nos. WO 99/20727, 20 WO 99/20726 and WO 99/20723 all filed on October 23, 1998 by The Procter & Gamble Company. In one embodiment, the protease variant includes the substitution set 101/103/104/159/232/236/245/248/252, such as 101G/103A/104I/159D/232V/236H/245R/248D/ 252K.

25 Also suitable for the present invention are proteases described in patent applications EP 251 446 and WO 91/06637, protease BLAP<sup>®</sup> described in WO91/02792 and their variants described in WO 95/23221.

30 See also a high pH protease from *Bacillus* sp. NCIMB 40338 described in WO 93/18140 A to Novo. Enzymatic detergents comprising protease, one or more other enzymes, and a reversible protease inhibitor are described in WO 92/03529 A to Novo. When desired, a protease having decreased adsorption and increased hydrolysis is available as described in WO 95/07791 to Procter & Gamble. A recombinant trypsin-like protease for detergents suitable herein is described in WO 94/25583 to Novo. Other suitable proteases are described in EP 516 200 by Unilever.

Commercially available proteases useful in the present invention are known as ESPERASE<sup>®</sup>, ALCALASE<sup>®</sup>, DURAZYM<sup>®</sup>, SAVINASE<sup>®</sup>, EVERLASE<sup>®</sup> and KANNASE<sup>®</sup>



all from Novo Nordisk A/S of Denmark, and as MAXATASE<sup>®</sup>, MAXACAL<sup>®</sup>, PROPERASE<sup>®</sup> and MAXAPEM<sup>®</sup> all from Genencor International (formerly Gist-Brocades of The Netherlands).

The cellulases usable in the present invention include both bacterial or fungal cellulase. Preferably, they will have a pH optimum of between 5 and 9.5. Suitable cellulases are disclosed in  
 5 U.S. Patent 4,435,307, Barbesgaard et al, which discloses fungal cellulase produced from *Humicola insolens*. Suitable cellulases are also disclosed in GB-A-2.075.028; GB-A-2.095.275 and DE-OS-2.247.832.

Examples of such cellulases are cellulases produced by a strain of *Humicola insolens* (*Humicola grisea* var. *thermoidea*), particularly the *Humicola* strain DSM 1800.

10 Other suitable cellulases are cellulases originated from *Humicola insolens* having a molecular weight of about 50KDa, an isoelectric point of 5.5 and containing 415 amino acids; and a ~43kD endoglucanase derived from *Humicola insolens*, DSM 1800, exhibiting cellulase activity; a preferred endoglucanase component has the amino acid sequence disclosed in PCT Patent Application No. WO 91/17243. Also suitable cellulases are the EGIII cellulases from *Trichoderma*  
 15 *longibrachiatum* described in WO94/21801, Genencor, published September 29, 1994. Especially suitable cellulases are the cellulases having color care benefits. Examples of such cellulases are cellulases described in European patent application No. 91202879.2, filed November 6, 1991 (Novo). Carezyme and Celluzyme (Novo Nordisk A/S) are especially useful. See also WO91/17243.

20 Peroxidase enzymes are known in the art, and include, for example, horseradish peroxidase, ligninase and haloperoxidase such as chloro- and bromo-peroxidase. Peroxidase-containing bleaching compositions are disclosed, for example, in U.S. Patent Nos. 5,576,282, 5,728,671 and 5,707,950, PCT International Applications WO 89/099813, WO89/09813 and in European Patent application EP No. 91202882.6, filed on November 6, 1991 and EP No.  
 25 96870013.8, filed February 20, 1996. Also suitable is the laccase enzyme.

Preferred enhancers are substituted phenothiazine and phenoxazine 10-Phenothiazinepropionic acid (PPT), 10-ethylphenothiazine-4-carboxylic acid (EPC), 10-phenoxazinepropionic acid (POP) and 10-methylphenoxazine (described in WO 94/12621) and substituted syringates (C3-C5 substituted alkyl syringates) and phenols. Sodium percarbonate or  
 30 perborate are preferred sources of hydrogen peroxide.

Said peroxidases are normally incorporated in the bleaching composition at levels from 0.0001% to 2% of active enzyme by weight of the bleaching composition.

Other preferred enzymes that can be included in the bleaching compositions of the present invention include lipases. Suitable lipase enzymes for detergent usage include those produced by  
 35 microorganisms of the *Pseudomonas* group, such as *Pseudomonas stutzeri* ATCC 19.154, as

disclosed in British Patent 1,372,034. Suitable lipases include those which show a positive immunological cross-reaction with the antibody of the lipase, produced by the microorganism *Pseudomonas fluorescent* IAM 1057. This lipase is available from Amano Pharmaceutical Co. Ltd., Nagoya, Japan, under the trade name Lipase P "Amano," hereinafter referred to as "Amano-P". Other suitable commercial lipases include Amano-CES, lipases ex *Chromobacter viscosum*, e.g. *Chromobacter viscosum* var. *lipolyticum* NRRLB 3673 from Toyo Jozo Co., Tagata, Japan; *Chromobacter viscosum* lipases from U.S. Biochemical Corp., U.S.A. and Disoynth Co., The Netherlands, and lipases ex *Pseudomonas gladioli*. Especially suitable lipases are lipases such as M1 LIPASE<sup>®</sup> and LIPOMAX<sup>®</sup> (Gist-Brocades) and LIPOLASE<sup>®</sup> and LIPOLASE ULTRA<sup>®</sup>(Novo) which have found to be very effective when used in combination with the compositions of the present invention.

Also suitable are cutinases [EC 3.1.1.50] which can be considered as a special kind of lipase, namely lipases which do not require interfacial activation. Addition of cutinases to bleaching compositions have been described in e.g. WO 88/09367 (Genencor).

The lipases and/or cutinases are normally incorporated in the bleaching composition at levels from 0.0001% to 2% of active enzyme by weight of the bleaching composition.

Known amylases ( $\alpha$  and/or  $\beta$ ) can be included for removal of carbohydrate-based stains. WO 94/02597, Novo Nordisk A/S published February 03, 1994, describes cleaning compositions which incorporate mutant amylases. See also WO94/18314, Genencor, published August 18, 1994 and WO95/10603, Novo Nordisk A/S, published April 20, 1995. Other amylases known for use in bleaching compositions include both  $\alpha$ - and  $\beta$ -amylases.  $\alpha$ -Amylases are known in the art and include those disclosed in US Pat. 5,003,257; EP 252,666; WO 91/00353; FR 2,676,456; EP 285,123; EP 525,610; EP 368,341; and British Patent Specification No. 1,296,839 (Novo). Other suitable amylase are stability-enhanced amylases including PURAFAC<sup>®</sup> OX AM<sup>®</sup> described in WO 94/18314, published August 18, 1994 and WO96/05295, Genencor, published February 22, 1996 and amylase variants from Novo Nordisk A/S, disclosed in WO 95/10603, published April 95.

Examples of commercial  $\alpha$ -amylases products are TERMAMYL<sup>®</sup>, BAN<sup>®</sup>, FUNGAMYL<sup>®</sup> and DURAMYL<sup>®</sup>, all available from Novo Nordisk A/S Denmark. WO95/26397 describes other suitable amylases :  $\alpha$ -amylases characterized by having a specific activity at least 25% higher than the specific activity of TERMAMYL<sup>®</sup> at a temperature range of 25°C to 55°C and at a pH value in the range of 8 to 10, measured by the Phadebas<sup>®</sup>  $\alpha$ -amylase activity assay. Other amylolytic enzymes with improved properties with respect to the activity level and the combination of thermostability and a higher activity level are described in WO95/35382.

The compositions of the present invention may also comprise a mannanase enzyme. Preferably, the mannanase is selected from the group consisting of: three mannans-degrading enzymes : EC 3.2.1.25 :  $\beta$ -mannosidase, EC 3.2.1.78 : Endo-1,4- $\beta$ -mannosidase, referred therein after as "mannanase" and EC 3.2.1.100 : 1,4- $\beta$ -mannobiosidase and mixtures thereof. (IUPAC Classification- Enzyme nomenclature, 1992 ISBN 0-12-227165-3 Academic Press).

More preferably, the treating compositions of the present invention, when a mannanase is present, comprise a  $\beta$ -1,4-Mannosidase (E.C. 3.2.1.78) referred to as Mannanase. The term "mannanase" or "galactomannanase" denotes a mannanase enzyme defined according to the art as officially being named mannan endo-1,4-beta-mannosidase and having the alternative names beta-mannanase and endo-1,4-mannanase and catalysing the reaction: random hydrolysis of 1,4-beta-D- mannosidic linkages in mannans, galactomannans, glucomannans, and galactoglucomannans.

In particular, Mannanases (EC 3.2.1.78) constitute a group of polysaccharases which degrade mannans and denote enzymes which are capable of cleaving polyose chains containing mannose units, i.e. are capable of cleaving glycosidic bonds in mannans, glucomannans, galactomannans and galactogluco-mannans. Mannans are polysaccharides having a backbone composed of  $\beta$ -1,4- linked mannose; glucomannans are polysaccharides having a backbone or more or less regularly alternating  $\beta$ -1,4 linked mannose and glucose; galactomannans and galactoglucomannans are mannans and glucomannans with  $\alpha$ -1,6 linked galactose sidebranches. These compounds may be acetylated.

The degradation of galactomannans and galactoglucomannans is facilitated by full or partial removal of the galactose sidebranches. Further the degradation of the acetylated mannans, glucomannans, galactomannans and galactogluco-mannans is facilitated by full or partial deacetylation. Acetyl groups can be removed by alkali or by mannan acetyl esterases. The oligomers which are released from the mannanases or by a combination of mannanases and  $\alpha$ -galactosidase and/or mannan acetyl esterases can be further degraded to release free maltose by  $\beta$ -mannosidase and/or  $\beta$ -glucosidase.

Mannanases have been identified in several *Bacillus* organisms. For example, Talbot et al., Appl. Environ. Microbiol., Vol.56, No. 11, pp. 3505-3510 (1990) describes a beta-mannanase derived from *Bacillus stearothermophilus* in dimer form having molecular weight of 162 kDa and an optimum pH of 5.5-7.5. Mendoza et al., World J. Microbiol. Biotech., Vol. 10, No. 5, pp. 551-555 (1994) describes a beta-mannanase derived from *Bacillus subtilis* having a molecular weight of 38 kDa, an optimum activity

at pH 5.0 and 55C and a pI of 4.8. JP-03047076 discloses a beta-mannanase derived from *Bacillus* sp., having a molecular weight of 373 kDa measured by gel filtration, an optimum pH of 8-10 and a pI of 5.3-5.4. JP-63056289 describes the production of an alkaline, thermostable beta-mannanase which hydrolyses beta-1,4-D-mannopyranoside bonds of e.g. mannans and produces manno-oligosaccharides. JP-63036774 relates to the *Bacillus* microorganism FERM P-8856 which produces beta-mannanase and beta-mannosidase at an alkaline pH. JP-08051975 discloses alkaline beta-mannanases from alkalophilic *Bacillus* sp. AM-001. A purified mannanase from *Bacillus amyloliquefaciens* useful in the bleaching of pulp and paper and a method of preparation thereof is disclosed in WO 97/11164. WO 91/18974 describes a hemicellulase such as a glucanase, xylanase or mannanase active at an extreme pH and temperature. WO 94/25576 discloses an enzyme from *Aspergillus aculeatus*, CBS 101.43, exhibiting mannanase activity which may be useful for degradation or modification of plant or algae cell wall material. WO 93/24622 discloses a mannanase isolated from *Trichoderma reesei* useful for bleaching lignocellulosic pulps. An hemicellulase capable of degrading mannan-containing hemicellulose is described in WO91/18974 and a purified mannanase from *Bacillus amyloliquefaciens* is described in WO97/11164.

Preferably, the mannanase enzyme will be an alkaline mannanase as defined below, more preferably, a mannanase originating from a bacterial source. Especially, the laundry detergent composition of the present invention will comprise an alkaline mannanase selected from the mannanase from the strain *Bacillus agaradhaerens* NICMB 40482; the mannanase from *Bacillus subtilis* strain 168, gene yght; the mannanase from *Bacillus* sp. I633 and/or the mannanase from *Bacillus* sp. AAI12. Most preferred mannanase for the inclusion in the detergent compositions of the present invention is the mannanase enzyme originating from *Bacillus* sp. I633 as described in the co-pending Danish patent application No. PA 1998 01340.

The terms "alkaline mannanase enzyme" is meant to encompass an enzyme having an enzymatic activity of at least 10%, preferably at least 25%, more preferably at least 40% of its maximum activity at a given pH ranging from 7 to 12, preferably 7.5 to 10.5. In one embodiment, the alkaline mannanase comprises the alkaline mannanase from *Bacillus agaradhaerens* NICMB 40482 is described in the co-pending U.S. patent application serial No. 09/111,256.

The mannanase, when present, is incorporated into the treating compositions of the present invention preferably at a level of from 0.0001% to 2%, more preferably from

0.0005% to 0.1%, most preferred from 0.001% to 0.02% pure enzyme by weight of the composition.

The compositions of the present invention may also comprise a xyloglucanase enzyme. Suitable xyloglucanases for the purpose of the present invention are enzymes exhibiting endoglucanase activity specific for xyloglucan, preferably at a level of from about 0.001% to about 1%, more preferably from about 0.01% to about 0.5%, by weight of the composition. As used herein, the term "endoglucanase activity" means the capability of the enzyme to hydrolyze 1,4- $\beta$ -D-glycosidic linkages present in any cellulosic material, such as cellulose, cellulose derivatives, lichenin,  $\beta$ -D-glucan, or xyloglucan. The endoglucanase activity may be determined in accordance with methods known in the art, examples of which are described in WO 94/14953 and hereinafter. One unit of endoglucanase activity (e.g. CMCU, AVIU, XGU or BGU) is defined as the production of 1  $\mu$ mol reducing sugar/min from a glucan substrate, the glucan substrate being, e.g., CMC (CMCU), acid swollen Avicell (AVIU), xyloglucan (XGU) or cereal  $\beta$ -glucan (BGU). The reducing sugars are determined as described in WO 94/14953 and hereinafter. The specific activity of an endoglucanase towards a substrate is defined as units/mg of protein.

More specifically, as used herein the term "specific for xyloglucan" means that the endoglucanase enzyme exhibits its highest endoglucanase activity on a xyloglucan substrate, and preferably less than 75% activity, more preferably less than 50% activity, most preferably less than about 25% activity, on other cellulose-containing substrates such as carboxymethyl cellulose, cellulose, or other glucans.

Preferably, the specificity of an endoglucanase towards xyloglucan is further defined as a relative activity determined as the release of reducing sugars at optimal conditions obtained by incubation of the enzyme with xyloglucan and the other substrate to be tested, respectively. For instance, the specificity may be defined as the xyloglucan to  $\beta$ -glucan activity (XGU/BGU), xyloglucan to carboxy methyl cellulose activity (XGU/CMCU), or xyloglucan to acid swollen Avicell activity (XGU/AVIU), which is preferably greater than about 50, such as 75, 90 or 100.

The term "derived from" as used herein refers not only to an endoglucanase produced by strain CBS 101.43, but also an endoglucanase encoded by a DNA sequence isolated from strain CBS 101.43 and produced in a host organism transformed with said DNA sequence. The term "homologue" as used herein indicates a polypeptide encoded by DNA which hybridizes to the same probe as the DNA coding for an endoglucanase enzyme specific for xyloglucan under certain specified conditions (such as presoaking in

5xSSC and prehybridizing for 1 h at -40°C in a solution of 5xSSC, 5xDenhardt's solution, and 50 µg of denatured sonicated calf thymus DNA, followed by hybridization in the same solution supplemented with 50 µCi 32-P-dCTP labelled probe for 18 h at -40°C and washing three times in 2xSSC, 0.2% SDS at 40°C for 30 minutes). More specifically, the term is intended to refer to a DNA sequence which is at least 70% homologous to any of the sequences shown above encoding an endoglucanase specific for xyloglucan, including at least 75%, at least 80%, at least 85%, at least 90% or even at least 95% with any of the sequences shown above. The term is intended to include modifications of any of the DNA sequences shown above, such as nucleotide substitutions which do not give rise to another amino acid sequence of the polypeptide encoded by the sequence, but which correspond to the codon usage of the host organism into which a DNA construct comprising any of the DNA sequences is introduced or nucleotide substitutions which do give rise to a different amino acid sequence and therefore, possibly, a different amino acid sequence and therefore, possibly, a different protein structure which might give rise to an endoglucanase mutant with different properties than the native enzyme. Other examples of possible modifications are insertion of one or more nucleotides into the sequence, addition of one or more nucleotides at either end of the sequence, or deletion of one or more nucleotides at either end or within the sequence.

Endoglucanase specific for xyloglucan useful in the present invention preferably is one which has a XGU/BGU, XGU/CMU and/or XGU/AVIU ratio (as defined above) of more than 50, such as 75, 90 or 100.

Furthermore, the endoglucanase specific for xyloglucan is preferably substantially devoid of activity towards β-glucan and/or exhibits at the most 25% such as at the most 10% or about 5%, activity towards carboxymethyl cellulose and/or Avicell when the activity towards xyloglucan is 100%. In addition, endoglucanase specific for xyloglucan of the invention is preferably substantially devoid of transferase activity, an activity which has been observed for most endoglucanases specific for xyloglucan of plant origin.

Endoglucanase specific for xyloglucan may be obtained from the fungal species *A. aculeatus*, as described in WO 94/14953. Microbial endoglucanases specific for xyloglucan has also been described in WO 94/14953. Endoglucanases specific for xyloglucan from plants have been described, but these enzymes have transferase activity and therefore must be considered inferior to microbial endoglucanases specific for xyloglucan whenever extensive degradation of xyloglucan is desirable. An additional advantage of a microbial enzyme is that it, in general, may be produced in higher amounts in a microbial host, than enzymes of other origins.

The xyloglucanase, when present, is incorporated into the treating compositions of the invention preferably at a level of from 0.0001% to 2%, more preferably from 0.0005% to 0.1%, most preferred from 0.001% to 0.02% pure enzyme by weight of the composition.

The above-mentioned enzymes may be of any suitable origin, such as vegetable, animal, bacterial, fungal and yeast origin. Purified or non-purified forms of these enzymes may be used. Also included by definition, are mutants of native enzymes. Mutants can be obtained e.g. by protein and/or genetic engineering, chemical and/or physical modifications of native enzymes. Common practice as well is the expression of the enzyme via host organisms in which the genetic material responsible for the production of the enzyme has been cloned.

Said enzymes are normally incorporated in the bleaching composition at levels from 0.0001% to 2% of active enzyme by weight of the bleaching composition. The enzymes can be added as separate single ingredients (prills, granulates, stabilized liquids, etc. containing one enzyme) or as mixtures of two or more enzymes (e.g. cogramulates).

Other suitable detergent ingredients that can be added are enzyme oxidation scavengers. Examples of such enzyme oxidation scavengers are ethoxylated tetraethylene polyamines.

A range of enzyme materials and means for their incorporation into synthetic bleaching compositions is also disclosed in WO 93/07263 and WO 93/07260 to Genencor International, WO 89/08694 to Novo, and U.S. 3,553,139, January 5, 1971 to McCarty et al. Enzymes are further disclosed in U.S. 4,101,457, Place et al, July 18, 1978, and in U.S. 4,507,219, Hughes, March 26, 1985. Enzyme materials useful for liquid detergent formulations, and their incorporation into such formulations, are disclosed in U.S. 4,261,868, Hora et al, April 14, 1981.

Enzyme Stabilizers - Enzymes for use in detergents can be stabilized by various techniques. Enzyme stabilization techniques are disclosed and exemplified in U.S. 3,600,319, EP 199,405 and EP 200,586. Enzyme stabilization systems are also described, for example, in U.S. 3,519,570. A useful *Bacillus*, sp. AC13 giving proteases, xylanases and cellulases, is described in WO 9401532. The enzymes employed herein can be stabilized by the presence of water-soluble sources of calcium and/or magnesium ions in the finished compositions which provide such ions to the enzymes. Suitable enzyme stabilizers and levels of use are described in U.S. Pat. Nos. 5,705,464, 5,710,115 and 5,576,282.

Builders - The detergent and bleaching compositions described herein preferably comprise one or more detergent builders or builder systems. When present, the compositions will typically comprise at least about 1% builder, preferably from about 5%, more preferably from about 10% to about 80%, preferably to about 50%, more preferably to about 30% by weight, of detergent builder. Lower or higher levels of builder, however, are not meant to be excluded.

Preferred builders for use in the detergent and bleaching compositions, particularly dishwashing compositions, described herein include, but are not limited to, water-soluble builder compounds, (for example polycarboxylates) as described in U.S. Patent Nos. 5,695,679, 5,705,464 and 5,710,115. Other suitable polycarboxylates are disclosed in U.S. Patent Nos. 4,144,226, 3,308,067 and 3,723,322. Preferred polycarboxylates are hydroxycarboxylates containing up to three carboxy groups per molecule, more particularly titrates.

Inorganic or P-containing detergent builders include, but are not limited to, the alkali metal, ammonium and alkanolammonium salts of polyphosphates (exemplified by the tripolyphosphates, pyrophosphates, and glassy polymeric meta-phosphates), phosphonates (see, for example, U.S. Patent Nos. 3,159,581; 3,213,030; 3,422,021; 3,400,148 and 3,422,137), phytic acid, silicates, carbonates (including bicarbonates and sesquicarbonates), sulphates, and aluminosilicates.

However, non-phosphate builders are required in some locales. Importantly, the compositions herein function surprisingly well even in the presence of the so-called "weak" builders (as compared with phosphates) such as citrate, or in the so-called "underbuilt" situation that may occur with zeolite or layered silicate builders.

Suitable silicates include the water-soluble sodium silicates with an  $\text{SiO}_2:\text{Na}_2\text{O}$  ratio of from about 1.0 to 2.8, with ratios of from about 1.6 to 2.4 being preferred, and about 2.0 ratio being most preferred. The silicates may be in the form of either the anhydrous salt or a hydrated salt. Sodium silicate with an  $\text{SiO}_2:\text{Na}_2\text{O}$  ratio of 2.0 is the most preferred. Silicates, when present, are preferably present in the detergent and bleaching compositions described herein at a level of from about 5% to about 50% by weight of the composition, more preferably from about 10% to about 40% by weight.

Partially soluble or insoluble builder compounds, which are suitable for use in the detergent and bleaching compositions, particularly granular detergent compositions, include, but are not limited to, crystalline layered silicates, preferably crystalline layered sodium silicates (partially water-soluble) as described in U.S. Patent No. 4,664,839, and sodium aluminosilicates (water-insoluble). When present in detergent and bleaching compositions, these builders are typically present at a level of from about 1% to 80% by weight, preferably from about 10% to 70% by weight, most preferably from about 20% to 60% by weight of the composition.

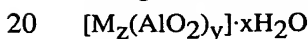
Crystalline layered sodium silicates having the general formula  $\text{NaMSi}_x\text{O}_{2x+1} \cdot y\text{H}_2\text{O}$  wherein M is sodium or hydrogen, x is a number from about 1.9 to about 4, preferably from about 2 to about 4, most preferably 2, and y is a number from about 0 to about 20, preferably 0 can be used in the compositions described herein. Crystalline layered sodium silicates of this type are disclosed in EP-A-0164514 and methods for their preparation are disclosed in DE-A-3417649 and



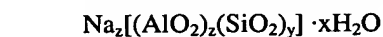
DE-A-3742043. The most preferred material is delta- $\text{Na}_2\text{SiO}_5$ , available from Hoechst AG as NaSKS-6 (commonly abbreviated herein as "SKS-6"). Unlike zeolite builders, the Na SKS-6 silicate builder does not contain aluminum. NaSKS-6 has the delta- $\text{Na}_2\text{SiO}_5$  morphology form of layered silicate. SKS-6 is a highly preferred layered silicate for use in the compositions described herein herein, but other such layered silicates, such as those having the general formula  $\text{NaMSi}_x\text{O}_{2x+1} \cdot y\text{H}_2\text{O}$  wherein M is sodium or hydrogen, x is a number from 1.9 to 4, preferably 2, and y is a number from 0 to 20, preferably 0 can be used in the compositions described herein. Various other layered silicates from Hoechst include NaSKS-5, NaSKS-7 and NaSKS-11, as the alpha, beta and gamma forms. As noted above, the delta- $\text{Na}_2\text{SiO}_5$  (NaSKS-6 form) is most preferred for use herein. Other silicates may also be useful such as for example magnesium silicate, which can serve as a crispening agent in granular formulations, as a stabilizing agent for oxygen bleaches, and as a component of suds control systems.

The crystalline layered sodium silicate material is preferably present in granular detergent compositions as a particulate in intimate admixture with a solid, water-soluble ionizable material. The solid, water-soluble ionizable material is preferably selected from organic acids, organic and inorganic acid salts and mixtures thereof.

Aluminosilicate builders are of great importance in most currently marketed heavy duty granular detergent compositions, and can also be a significant builder ingredient in liquid detergent formulations. Aluminosilicate builders have the empirical formula:

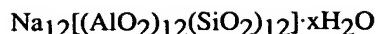


wherein z and y are integers of at least 6, the molar ratio of z to y is in the range from 1.0 to about 0.5, and x is an integer from about 15 to about 264. Preferably, the aluminosilicate builder is an aluminosilicate zeolite having the unit cell formula:



wherein z and y are at least 6; the molar ratio of z to y is from 1.0 to 0.5 and x is at least 5, preferably 7.5 to 276, more preferably from 10 to 264. The aluminosilicate builders are preferably in hydrated form and are preferably crystalline, containing from about 10% to about 28%, more preferably from about 18% to about 22% water in bound form.

These aluminosilicate ion exchange materials can be crystalline or amorphous in structure and can be naturally-occurring aluminosilicates or synthetically derived. A method for producing aluminosilicate ion exchange materials is disclosed in U.S. 3,985,669. Preferred synthetic crystalline aluminosilicate ion exchange materials useful herein are available under the designations Zeolite A, Zeolite B, Zeolite P, Zeolite X, Zeolite MAP and Zeolite HS and mixtures thereof. In an especially preferred embodiment, the crystalline aluminosilicate ion exchange material has the formula:



wherein x is from about 20 to about 30, especially about 27. This material is known as Zeolite A. Dehydrated zeolites (x = 0 - 10) may also be used herein. Preferably, the aluminosilicate has a particle size of about 0.1-10 microns in diameter. Zeolite X has the formula:



Citrate builders, e.g., citric acid and soluble salts thereof (particularly sodium salt), are polycarboxylate builders of particular importance for heavy duty liquid detergent formulations due to their availability from renewable resources and their biodegradability. Citrates can also be used in granular compositions, especially in combination with zeolite and/or layered silicate builders. Oxydisuccinates are also especially useful in such compositions and combinations.

Also suitable in the detergent compositions described herein are the 3,3-dicarboxy-4-oxa-1,6-hexanedioates and the related compounds disclosed in U.S. 4,566,984. Useful succinic acid builders include the C<sub>5</sub>-C<sub>20</sub> alkyl and alkenyl succinic acids and salts thereof. A particularly preferred compound of this type is dodecenylsuccinic acid. Specific examples of succinate builders include: laurylsuccinate, myristylsuccinate, palmitylsuccinate, 2-dodecenylsuccinate (preferred), 2-pentadecenylsuccinate, and the like. Laurylsuccinates are the preferred builders of this group, and are described in European Patent Application 86200690.5/0,200,263, published November 5, 1986.

Fatty acids, e.g., C<sub>12</sub>-C<sub>18</sub> monocarboxylic acids, can also be incorporated into the compositions alone, or in combination with the aforesaid builders, especially citrate and/or the succinate builders, to provide additional builder activity. Such use of fatty acids will generally result in a diminution of sudsing, which should be taken into account by the formulator.

Dispersants - One or more suitable polyalkyleneimine dispersants may be incorporated into the cleaning compositions of the present invention. Examples of such suitable dispersants can be found in European Patent Application Nos. 111,965, 111,984, and 112,592; U.S. Patent Nos. 4,597,898, 4,548,744, and 5,565,145. However, any suitable clay/soil dispersant or anti-redeposition agent can be used in the laundry compositions of the present invention.

In addition, polymeric dispersing agents which include polymeric polycarboxylates and polyethylene glycols, are suitable for use in the present invention. Unsaturated monomeric acids that can be polymerized to form suitable polymeric polycarboxylates include acrylic acid, maleic acid (or maleic anhydride), fumaric acid, itaconic acid, aconitic acid, mesaconic acid, citraconic acid and methylenemalononic acid. Particularly suitable polymeric polycarboxylates can be derived from acrylic acid. Such acrylic acid-based polymers which are useful herein are the water-soluble salts of polymerized acrylic acid. The average molecular weight of such polymers in the acid form preferably ranges from about 2,000 to 10,000, more preferably from about 4,000 to 7,000 and

most preferably from about 4,000 to 5,000. Water-soluble salts of such acrylic acid polymers can include, for example, the alkali metal, ammonium and substituted ammonium salts. Soluble polymers of this type are known materials. Use of polyacrylates of this type in detergent compositions has been disclosed, for example, in U.S. 3,308,067.

5           Acrylic/maleic-based copolymers may also be used as a preferred component of the dispersing/anti-redeposition agent. Such materials include the water-soluble salts of copolymers of acrylic acid and maleic acid. The average molecular weight of such copolymers in the acid form preferably ranges from about 2,000 to 100,000, more preferably from about 5,000 to 75,000, most preferably from about 7,000 to 65,000. The ratio of acrylate to maleate segments in such  
10 copolymers will generally range from about 30:1 to about 1:1, more preferably from about 10:1 to 2:1. Water-soluble salts of such acrylic acid/maleic acid copolymers can include, for example, the alkali metal, ammonium and substituted ammonium salts. Soluble acrylate/maleate copolymers of this type are known materials which are described in European Patent Application No. 66915, published December 15, 1982, as well as in EP 193,360, published September 3, 1986, which also  
15 describes such polymers comprising hydroxypropylacrylate. Still other useful dispersing agents include the maleic/acrylic/vinyl alcohol terpolymers. Such materials are also disclosed in EP 193,360, including, for example, the 45/45/10 terpolymer of acrylic/maleic/vinyl alcohol.

Another polymeric material which can be included is polyethylene glycol (PEG). PEG can exhibit dispersing agent performance as well as act as a clay soil removal-antiredeposition  
20 agent. Typical molecular weight ranges for these purposes range from about 500 to about 100,000, preferably from about 1,000 to about 50,000, more preferably from about 1,500 to about 10,000.

Polyaspartate and polyglutamate dispersing agents may also be used, especially in conjunction with zeolite builders. Dispersing agents such as polyaspartate preferably have a  
25 molecular weight (avg.) of about 10,000.

Soil Release Agents - The compositions according to the present invention may optionally comprise one or more soil release agents. If utilized, soil release agents will generally comprise from about 0.01%, preferably from about 0.1%, more preferably from about 0.2% to about 10%, preferably to about 5%, more preferably to about 3% by weight, of the composition. Nonlimiting  
30 examples of suitable soil release polymers are disclosed in: U.S. Patent Nos. 5,728,671; 5,691,298; 5,599,782; 5,415,807; 5,182,043; 4,956,447; 4,976,879; 4,968,451; 4,925,577; 4,861,512; 4,877,896; 4,771,730; 4,711,730; 4,721,580; 4,000,093; 3,959,230; and 3,893,929; and European Patent Application 0 219 048.

Further suitable soil release agents are described in U.S. Patent Nos. 4,201,824; 4,240,918; 4,525,524; 4,579,681; 4,220,918; and 4,787,989; EP 279,134 A; EP 457,205 A; and DE 2,335,044.

Chelating Agents - The compositions of the present invention herein may also optionally contain a chelating agent which serves to chelate metal ions and metal impurities which would otherwise tend to deactivate the bleaching agent(s). Useful chelating agents can include amino carboxylates, phosphonates, amino phosphonates, polyfunctionally-substituted aromatic chelating agents and mixtures thereof. Further examples of suitable chelating agents and levels of use are described in U.S. Pat. Nos. 5,705,464, 5,710,115, 5,728,671 and 5,576,282.

The compositions herein may also contain water-soluble methyl glycine diacetic acid (MGDA) salts (or acid form) as a chelant or co-builder useful with, for example, insoluble builders such as zeolites, layered silicates and the like.

If utilized, these chelating agents will generally comprise from about 0.1% to about 15%, more preferably from about 0.1% to about 3.0% by weight of the detergent compositions herein.

Suds suppressor - Another optional ingredient is a suds suppressor, exemplified by silicones, and silica-silicone mixtures. Examples of suitable suds suppressors are disclosed in U.S. Patent Nos. 5,707,950 and 5,728,671. These suds suppressors are normally employed at levels of from 0.001% to 2% by weight of the composition, preferably from 0.01% to 1% by weight.

Softening agents - Fabric softening agents can also be incorporated into laundry detergent compositions in accordance with the present invention. Inorganic softening agents are exemplified by the smectite clays disclosed in GB-A-1 400 898 and in U.S. 5,019,292. Organic softening agents include the water insoluble tertiary amines as disclosed in GB-A-1 514 276 and EP-B-011 340 and their combination with mono C12-C14 quaternary ammonium salts are disclosed in EP-B-026 527 and EP-B-026 528 and di-long-chain amides as disclosed in EP-B-0 242 919. Other useful organic ingredients of fabric softening systems include high molecular weight polyethylene oxide materials as disclosed in EP-A-0 299 575 and 0 313 146.

Particularly suitable fabric softening agents are disclosed in U.S. Patent Nos. 5,707,950 and 5,728,673.

Levels of smectite clay are normally in the range from 2% to 20%, more preferably from 5% to 15% by weight, with the material being added as a dry mixed component to the remainder of the formulation. Organic fabric softening agents such as the water-insoluble tertiary amines or dilong chain amide materials are incorporated at levels of from 0.5% to 5% by weight, normally from 1% to 3% by weight whilst the high molecular weight polyethylene oxide materials and the water soluble cationic materials are added at levels of from 0.1% to 2%, normally from 0.15% to 1.5% by weight. These materials are normally added to the spray dried portion of the composition,

although in some instances it may be more convenient to add them as a dry mixed particulate, or spray them as molten liquid on to other solid components of the composition.

Biodegradable quaternary ammonium compounds as described in EP-A-040 562 and EP-A-239 910 have been presented as alternatives to the traditionally used di-long alkyl chain ammonium chlorides and methyl sulfates.

Non-limiting examples of softener-compatible anions for the quaternary ammonium compounds and amine precursors include chloride or methyl sulfate.

Dye transfer inhibition - The detergent compositions of the present invention can also include compounds for inhibiting dye transfer from one fabric to another of solubilized and suspended dyes encountered during fabric laundering and conditioning operations involving colored fabrics.

*Polymeric dye transfer inhibiting agents*

The detergent compositions according to the present invention can also comprise from 0.001% to 10 %, preferably from 0.01% to 2%, more preferably from 0.05% to 1% by weight of polymeric dye transfer inhibiting agents. Said polymeric dye transfer inhibiting agents are normally incorporated into detergent compositions in order to inhibit the transfer of dyes from colored fabrics onto fabrics washed therewith. These polymers have the ability to complex or adsorb the fugitive dyes washed out of dyed fabrics before the dyes have the opportunity to become attached to other articles in the wash.

Especially suitable polymeric dye transfer inhibiting agents are polyamine N-oxide polymers, copolymers of N-vinylpyrrolidone and N-vinylimidazole, polyvinylpyrrolidone polymers, polyvinylloxazolidones and polyvinylimidazoles or mixtures thereof. Examples of such dye transfer inhibiting agents are disclosed in U.S. Patent Nos. 5,707,950 and 5,707,951.

Additional suitable dye transfer inhibiting agents include, but are not limited to, cross-linked polymers. Cross-linked polymers are polymers whose backbone are interconnected to a certain degree; these links can be of chemical or physical nature, possibly with active groups on the backbone or on branches; cross-linked polymers have been described in the Journal of Polymer Science, volume 22, pages 1035-1039.

In one embodiment, the cross-linked polymers are made in such a way that they form a three-dimensional rigid structure, which can entrap dyes in the pores formed by the three-dimensional structure. In another embodiment, the cross-linked polymers entrap the dyes by swelling. Such cross-linked polymers are described in the co-pending European patent application 94870213.9.

Addition of such polymers also enhances the performance of the enzymes according to the invention.

pH and Buffering Variation - Many of the detergent and bleaching compositions described herein will be buffered, i.e., they are relatively resistant to pH drop in the presence of acidic soils. However, other compositions herein may have exceptionally low buffering capacity, or may be substantially unbuffered. Techniques for controlling or varying pH at recommended usage levels more generally include the use of not only buffers, but also additional alkalis, acids, pH-jump systems, dual compartment containers, etc., and are well known to those skilled in the art.

The preferred ADD compositions herein comprise a pH-adjusting component selected from water-soluble alkaline inorganic salts and water-soluble organic or inorganic builders as described in U.S. Patent Nos. 5,705,464 and 5,710,115.

Material Care Agents - The preferred ADD compositions may contain one or more material care agents which are effective as corrosion inhibitors and/or anti-tarnish aids as described in U.S. Patent Nos. 5,705,464, 5,710,115 and 5,646,101.

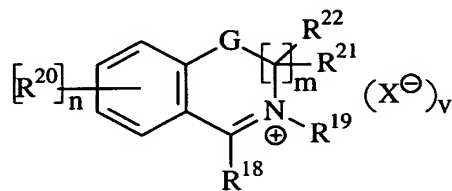
When present, such protecting materials are preferably incorporated at low levels, e.g., from about 0.01% to about 5% of the ADD composition.

Other Materials - Detergent ingredients or adjuncts optionally included in the instant compositions can include one or more materials for assisting or enhancing cleaning performance, treatment of the substrate to be cleaned, or designed to improve the aesthetics of the compositions. Adjuncts which can also be included in compositions of the present invention, at their conventional art-established levels for use (generally, adjunct materials comprise, in total, from about 30% to about 99.9%, preferably from about 70% to about 95%, by weight of the compositions), include other active ingredients such as non-phosphate builders, color speckles, silvercare, anti-tarnish and/or anti-corrosion agents, dyes, fillers, germicides, alkalinity sources, hydrotropes, anti-oxidants, perfumes, solubilizing agents, carriers, processing aids, pigments, and pH control agents as described in U.S. Patent Nos. 5,705,464, 5,710,115, 5,698,504, 5,695,679, 5,686,014 and 5,646,101.

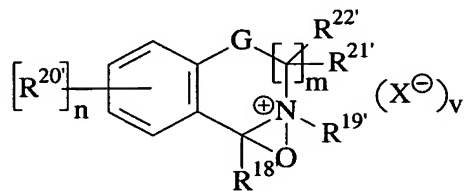
Methods of Cleaning - In addition to the methods for cleaning fabrics, dishes and other hard surfaces, and body parts by personal cleansing, described herein, the invention herein also encompasses a laundering pretreatment process for fabrics which have been soiled or stained comprising directly contacting said stains and/or soils with a highly concentrated form of the bleaching composition set forth above prior to washing such fabrics using conventional aqueous washing solutions. Preferably, the bleaching composition remains in contact with the soil/stain for a period of from about 30 seconds to 24 hours prior to washing the pretreated soiled/stained substrate in conventional manner. More preferably, pretreatment times will range from about 1 to 180 minutes.

The following examples are meant to exemplify compositions of the present invention, but are not necessarily meant to limit or otherwise define the scope of the invention.

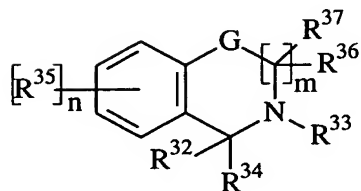
In the following examples some abbreviations known to those of ordinary skill in the art are used, consistent with the disclosure set forth herein. The organic catalysts are preferably present in the following at a level of from about 0.1 ppm (0.01% by weight) to about 10 ppm (1.0% by weight). More preferably, the organic catalysts are present in the following at a level of from about 0.25 ppm (0.025% by weight) to about 2.5 ppm (0.25% by weight). The organic catalysts in the following examples can be any of the organic catalysts described hereinbefore including, but not limited to, the organic catalysts as set forth below and as used according to the examples below.



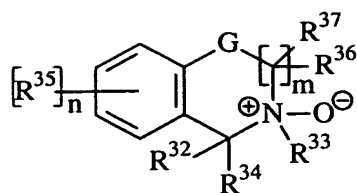
[XI]



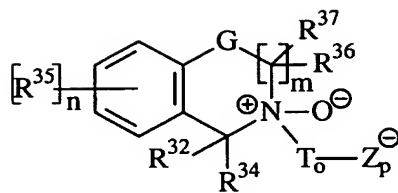
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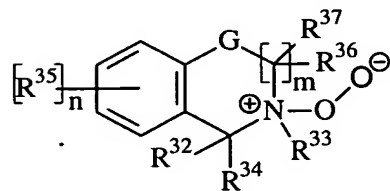
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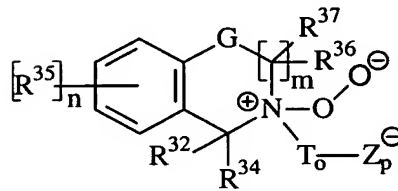
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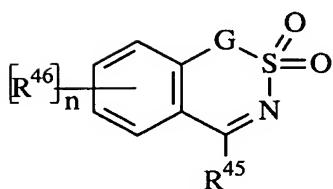
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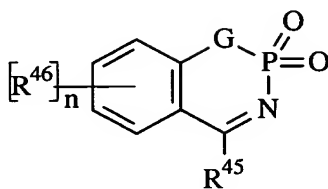
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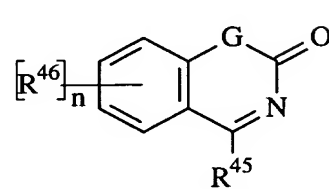
[XX]



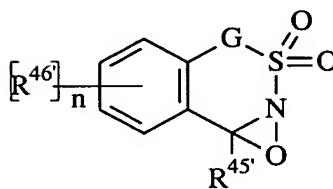
[XXVIIIa]



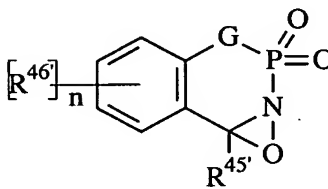
[XXVIIIb]



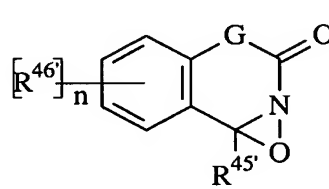
[XXIX]



[XXXIa]



[XXXIb]



[XXXII]

wherein the substituents for structures [XI] to [XXXII] are as defined hereinabove. Preferably, the organic catalyst compounds have one or more of the formulas: [XI] to [XIV] as defined immediately hereinabove. More preferably, the organic catalyst compounds have one or more of the formulas: [XI] and/or [XIII] as defined immediately hereinabove.

## FORMULATION EXAMPLES

### EXAMPLE I



Bleaching detergent compositions having the form of granular laundry detergents are exemplified by the following formulations.

	<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>	<u>E</u>
Organic Catalyst*	0.05	0.01	0.13	0.04	0.07
Conventional Activator (NOBS)	0.00	2.00	1.20	0.70	0.00
Conventional Activator (TAED)	3.00	0.00	2.00	0.00	0.00
Conventional Activator (NACA-OBS)	3.00	0.00	0.00	0.00	2.20
Sodium Percarbonate	5.30	0.00	0.00	4.00	0.00
Sodium Perborate Monohydrate	0.00	5.30	3.60	0.00	4.30
Linear Alkylbenzenesulfonate	12.00	0.00	12.00	0.00	21.00
C45AE0.6S	0.00	15.00	0.00	15.00	0.00
C2 Dimethylamine N-Oxide	0.00	2.00	0.00	2.00	0.00
C12 Coco Amidopropyl Betaine	1.50	0.00	1.50	0.00	0.00
Palm N- Methyl Glucamide	1.70	2.00	1.70	2.00	0.00
C12 Dimethylhydroxyethyl- ammonium Chloride	1.50	0.00	1.50	0.00	0.00
AE23-6.5T	2.50	3.50	2.50	3.50	1.00
C25E3S	4.00	0.00	4.00	0.00	0.00
Sodium Tripolyphosphate	25.00	25.00	15.00	15.00	25.00
Zeolite A	0.00	0.00	0.00	0.00	0.00
Acrylic Acid / Maleic Acid Copolymer	0.00	0.00	0.00	0.00	1.00
Polyacrylic Acid, partially neutralized	3.00	3.00	3.00	3.00	0.00
Soil Release Agent	0.00	0.00	0.50	0.40	0.00
Carboxymethylcellulose	0.40	0.40	0.40	0.40	0.40
Sodium Carbonate	2.00	2.00	2.00	0.00	8.00
Sodium Silicate	3.00	3.00	3.00	3.00	6.00
Sodium Bicarbonate	5.00	5.00	5.00	5.00	5.00
Savinase (4T)	1.00	1.00	1.00	1.00	0.60

Termamyl (60T)	0.40	0.40	0.40	0.40	0.40
Lipolase (100T)	0.12	0.12	0.12	0.12	0.12
Carezyme(5T)	0.15	0.15	0.15	0.15	0.15
Diethylenetriaminepenta (methylenephosphonic Acid)	1.60	1.60	1.60	1.60	0.40
Brightener	0.20	0.20	0.20	0.05	0.20
Sulfonated Zinc	0.50	0.00	0.25	0.00	0.00
Phthalocyanine Photobleach					
MgSO <sub>4</sub>	2.20	2.20	2.20	2.20	0.64
Na <sub>2</sub> SO <sub>4</sub>	balance	balance	balance	balance	balance

\* Any of the organic catalysts described herein, preferably a cationic organic catalyst.

- 5 Any of the above compositions is used to launder fabrics at a concentration of 3500 ppm in water, 25 °C, and a 15:1 water:cloth ratio. The typical pH is about 9.5 but can be can be adjusted by altering the proportion of acid to Na- salt form of alkylbenzenesulfonate.

#### EXAMPLE II

- 10 Bleaching detergent compositions having the form of granular laundry detergents are exemplified by the following formulations.

	<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>	<u>E</u>
Organic Catalyst *	0.06	0.34	0.14	0.14	0.20
Sodium Percarbonate	5.30	0.00	0.00	0.00	0.00
Sodium Perborate	0.00	9.00	17.60	9.00	9.00
Monohydrate					
Linear	21.00	12.00	0.00	12.00	12.00
Alkylbenzenesulfonate					
C45AE0.6S	0.00	0.00	15.00	0.00	0.00
C2 Dimethylamine N-Oxide	0.00	0.00	2.00	0.00	0.00
C12 Coco Amidopropyl	0.00	1.50	0.00	1.50	1.50
Betaine					
Palm N- Methyl Glucamide	0.00	1.70	2.00	1.70	1.70
C12	1.00	1.50	0.00	1.50	1.50
Dimethylhydroxyethylammo nium Chloride					

AE23-6.5T	0.00	2.50	3.50	2.50	2.50
C25E3S	0.00	4.00	0.00	4.00	4.00
Conventional Activator (NOBS)	0.00	0.00	0.00	1.00	0.00
Conventional Activator (TAED)	1.80	1.00	2.50	3.00	1.00
Sodium Tripolyphosphate	25.00	15.00	25.00	15.00	15.00
Zeolite A	0.00	0.00	0.00	0.00	0.00
Acrylic Acid / Maleic Acid Copolymer	0.00	0.00	0.00	0.00	0.00
Polyacrylic Acid, partially neutralized	0.00	3.00	3.00	3.00	3.00
Soil Release Agent	0.30	0.50	0.00	0.50	0.50
Carboxymethylcellulose	0.00	0.40	0.40	0.40	0.40
Sodium Carbonate	0.00	2.00	2.00	2.00	2.00
Sodium Silicate	6.00	3.00	3.00	3.00	3.00
Sodium Bicarbonate	2.00	5.00	5.00	5.00	5.00
Savinase (4T)	0.60	1.00	1.00	1.00	1.00
Termamyl (60T)	0.40	0.40	0.40	0.40	0.40
Lipolase (100T)	0.12	0.12	0.12	0.12	0.12
Carezyme(5T)	0.15	0.15	0.15	0.15	0.15
Diethylenetriaminepenta(met hylene phosphonic Acid)	0.40	0.00	1.60	0.00	0.00
Brightener	0.20	0.30	0.20	0.30	0.30
Sulfonated Zinc	0.25	0.00	0.00	0.00	0.00
Phthalocyanine Photobleach					
MgSO <sub>4</sub>	0.64	0.00	2.20	0.00	0.00
Na <sub>2</sub> SO <sub>4</sub>	balance	balance	balance	balance	balance

\*Any of the organic catalysts described herein, preferably a cationic organic catalyst, more preferably *N-tert*-butyl-3,4-dihydroisoquinolinium tetraphenylborate.

- 5 Any of the above compositions is used to launder fabrics at a concentration of 3500 ppm in water, 25°C, and a 15:1 water:cloth ratio. The typical pH is about 9.5 but can be adjusted by altering the proportion of acid to Na- salt form of alkylbenzenesulfonate.

**EXAMPLE III**

A bleaching detergent powder comprises the following ingredients:

Component	Weight %
Organic Catalyst*	0.07
TAED	2.0
Sodium Perborate Tetrahydrate	10
C <sub>12</sub> linear alkyl benzene sulfonate	8.0
Phosphate (as sodium tripolyphosphate)	9.0
Sodium Carbonate	20
Talc	15
Brightener, perfume	0.3
Sodium Chloride	25
Water and Minors	Balance to 100%

- \* Any organic catalyst described herein, preferably a cationic organic catalyst, more preferably 2-(3-sulfonato)propyl-4,5-dihydro-3H-2-benzazepine

**EXAMPLE IV**

- A laundry bar suitable for hand-washing soiled fabrics is prepared by standard extrusion processes and comprises the following:

Component	Weight %
Organic Catalyst <sup>1</sup>	0.2
TAED	1.7
NOBS	0.2
Sodium Perborate Tetrahydrate	12
C <sub>12</sub> linear alkyl benzene sulfonate	30
Phosphate (as sodium tripolyphosphate)	10
Sodium carbonate	5
Sodium pyrophosphate	7
Coconut monoethanolamide	2
Zeolite A (0.1-10 micron)	5

Carboxymethylcellulose	0.2
Polyacrylate (m.w. 1400)	0.2
Brightener, perfume	0.2
Protease	0.3
CaSO <sub>4</sub>	1
MgSO <sub>4</sub>	1
Water	4
Filler <sup>2</sup>	Balance to 100%

<sup>1</sup> Any organic catalyst described herein, preferably a cationic organic catalyst, more preferably 3,4-dihydroisoquinolinium tetrafluoroborate

<sup>2</sup> Can be selected from convenient materials such as CaCO<sub>3</sub>, talc, clay, silicates, and the like. Acidic fillers can be used to reduce pH

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#### EXAMPLE V

A laundry detergent composition suitable for machine use is prepared by standard methods and comprises the following composition:

10	<u>Component</u>	<u>Weight%</u>
	Organic Catalyst*	0.82
	TAED	7.20
	Sodium Perborate Tetrahydrate	9.2
	Sodium Carbonate	23.74
15	Anionic surfactant	14.80
	Alumino Silicate	21.30
	Silicate	1.85
	Diethylenetriaminepentacetic acid	0.43
	Polyacrylic acid	2.72
20	Brightener	0.23
	Polyethylene glycol solids	1.05
	Sulfate	8.21
	Perfume	0.25
	Water	7.72
25	Processing aid	0.10
	Miscellaneous	0.43

\* Any organic catalyst described herein, preferably a cationic organic catalyst, more preferably N-benzyl-1,2-oxy-1,2,3,4-tetrahydro-6,7-dimethoxyisoquinolinium chloride

5 The composition is used to launder fabrics at a concentration in solution of about 1000 ppm at a temperature of 20-40°C and a water to fabric ratio of about 20:1.

#### EXAMPLE VI

Component	Weight %
Organic Catalyst*	1.0
TAED	10.0
Sodium Perborate Tetrahydrate	8.0
Sodium Carbonate	21.0
Anionic surfactant	12.0
Alumino Silicate	18.0
Diethylenetriaminepentacetic acid	0.3
Nonionic surfactant	0.5
Polyacrylic acid	2.0
Brightener	0.3
Sulfate	17.0
Perfume	0.25
Water	6.7
Miscellaneous	2.95

10 \* Any organic catalyst described herein, preferably a cationic organic catalyst, more preferably N-cyclohexylmethyl-1-hydroxy-4-methyl-1,2,3,4-tetrahydroisoquinoline

The composition is used as a laundry auxiliary for laundering fabrics at a concentration in solution of about 850 ppm at a temperature of 20-40°C and a water to fabric ratio of about 20:1.

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#### EXAMPLE VII

A bleaching composition suitable for use in high suds phosphate geographies has the formula:

Component	A (%wt)	B (%wt)
Organic Catalyst*	0.02	0.018

	NOBS	1.90	2.00
	Sodium Perborate Tetrahydrate	2.25	3.00
	Sodium Carbonate	13.00	13.00
	Anionic surfactant	19.00	19.00
5	Cationic surfactant	0.60	0.60
	Nonionic surfactant	-	0.40
	Sodium Tripolyphosphate	22.50	22.50
	Diethylenetriaminepentacetic acid	0.90	0.90
	Acrylic acid/Maleic acid copolymer	0.90	0.90
10	Carboxymethylcellulose	0.40	0.40
	Protease	0.70	0.70
	Amylase	0.36	0.36
	Cellulase	0.35	0.35
	Brightener	0.16	0.18
15	Magnesium sulfate	0.70	0.70
	Water	3.0	1.0
	Sodium sulfate	Balance	Balance

\*Any of the organic catalysts described herein, preferably a cationic organic catalyst.

The composition is used as a laundry auxiliary for laundering fabrics at a concentration in solution of about 850 ppm at a temperature of 20-40°C and a water to fabric ratio of about 20:1.

The compositions of the present invention can be suitably prepared by any process chosen by the formulator, non-limiting examples of which are described in U.S. 5,691,297 Nassano et al., issued November 11, 1997; U.S. 5,574,005 Welch et al., issued November 12, 1996; U.S. 5,569,645 Dinniwel et al., issued October 29, 1996; U.S. 5,565,422 Del Greco et al., issued October 15, 1996; U.S. 5,516,448 Capecci et al., issued May 14, 1996; U.S. 5,489,392 Capecci et al., issued February 6, 1996; U.S. 5,486,303 Capecci et al., issued January 23, 1996 all of which are incorporated herein by reference.

In addition to the above examples, the organic catalyst compounds of the present invention can be formulated into any suitable laundry detergent composition, non-limiting examples of which are described in U.S. 5,679,630 Baeck et al., issued October 21, 1997; U.S. 5,565,145 Watson et al., issued October 15, 1996; U.S. 5,478,489 Fredj et al., issued December 26, 1995; U.S. 5,470,507 Fredj et al., issued November 28, 1995; U.S. 5,466,802 Panandiker et

al., issued November 14, 1995; U.S. 5,460,752 Fredj et al., issued October 24, 1995; U.S. 5,458,810 Fredj et al., issued October 17, 1995; U.S. 5,458,809 Fredj et al., issued October 17, 1995; U.S. 5,288,431 Huber et al., issued February 22, 1994 all of which are incorporated herein by reference.

- 5           Having described the present invention in detail with reference to preferred embodiments and examples, it will be clear to those skilled in the art that various changes and modifications may be made without departing from the scope of the invention, and the invention is not to be considered limited to what is described in the specification.

WHAT IS CLAIMED IS:

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